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LOW TEMPERATURE PHYSICS

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PREFACE

As the physics of low temperatures embraces practically every branch of the subject, it is quite impossible to deal with the whole of the available material in a short monograph. It has therefore been necessary to make a most rigid selection, and to treat in detail only a few sections of the subject selected for their particular interest. Further, the subject matter of this book is in general restricted to temperatures not higher than that of liquid air, and deals mainly with that range of temperature, 1°-20° K, which is accessible only in the specially equipped cryogenic laboratories.

Although the pioneer work of Dewar and of Travers was carried out in England, scientific research at very low temperatures has been completely in abeyance in this country during the last twenty-five years. It is therefore a matter for satisfaction to note that interest in the subject has been revived recently, and the facilities for such work have been greatly improved. Liquid hydrogen is now available at the new Mond Laboratory of the Royal Society at Cambridge, at the Clarendon Laboratory at Oxford, and at the Wills Laboratory, University of Bristol. A small helium liquefier of the type described by Simon and Ahlberg is in operation at Oxford, and apparatus for the liquefaction of helium on a fairly large scale has been installed at Cambridge.

I am greatly indebted to Professor A. M. Tyndall and to several colleagues on the staff of the Wills Laboratory for their continued interest and for numerous valuable discussions during the preparation of this book.

L. C. J.

H. H. Wills Physical Laboratory,
The University, Bristol.

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LOW TEMPERATURE PHYSICS

CHAPTER I

THE PRODUCTION OF LOW TEMPERATURES

THE LIQUEFACTION OF AIR, HYDROGEN AND HELIUM

ALL physical experiments at very low temperatures involve the use of liquefied (or solidified) gases in some way or other. The liquefaction of gases is thus an important branch of low temperature physics, and the principles underlying the methods employed will therefore be discussed briefly, with special reference to the cases of air, hydrogen and helium. With the aid of these three liquefied gases it is possible directly or indirectly to experiment over the whole range from room temperature down to 1° K., or even lower.

Apart from the now obsolete cascade process, there are two types of method available for the large scale liquefaction of air (and hydrogen and helium), that which employs the Joule-Thomson effect (expansion of a gas with the performance of " internal " work) to produce the necessary cooling (Linde, Hampson), and that which employs in part at least the reversible expansion of the gas with the performance of " external " work (Claude, Heylandt).

" INTERNAL WORK " METHODS OF GAS LIQUEFACTION

The essentials of a liquefier using the Joule-Thomson effect are shown diagrammatically in Fig. 1. Compressed gas enters the inner tube of the "Heat interchanger" H at a pressure p_A and temperature T_A. It then expands at the valve V to a pressure p_B and the temperature falls on account of the performance by the gas of "internal work" in expanding against the forces of attraction between the molecules. The cooled expanded gas then passes up the outer tube of the interchanger, cooling the incoming compressed gas as it does so. The expanded gas leaves the liquefier at the pressure p_B and temperature T_B (T_B is nearly equal to T_A if the interchanger is efficient). The cooler compressed gas expands at V, and is thereby further cooled and so on until the temperature at the lower end of the interchanger has fallen by this "regenerative" process sufficiently low for the gas to liquefy. A part of the expanded gas will then liquefy and collect at C (temperature = T_C).

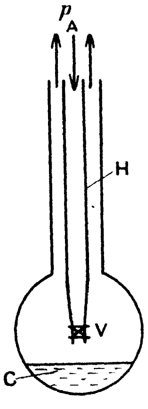

Fig. 1.

In such an expansion, provided there is no appreciable change in kinetic energy of the gas or after any change of kinetic energy has subsided, the "total heat" or "enthalpy" H of the gas before and after expansion remains constant, since the process takes place adiabatically, no heat being allowed to enter the system from outside. We therefore have *

$$H_A = U_A + p_A v_A = H_B = U_B + p_B v_B \qquad (1)$$

(U = internal energy, p = pressure, v = volume per unit mass).

Theory indicates that the change of temperature dT which results when the pressure of a gas changes by an amount dp on passing a throttle or expansion valve is given by

---

* For the thermodynamical theory of the Joule-Thomson effect and its "inversion," see Porter, "Thermodynamics," Methuen's Monographs on Physical Subjects.

$$\frac{dT}{dp}=\frac{1}{C_p}\left(T\left(\frac{\partial v}{\partial T}\right)_p-v\right)=\frac{T^2}{C_p}\frac{\partial}{\partial T}\left(\frac{v}{T}\right)=-\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T \quad (2)$$

(C_p = specific heat of gas at constant pressure).

The change of temperature dT is known as the "differential Joule-Thomson effect," and as appears from (2) its sign depends on the sign of $\left(T\left(\frac{\partial v}{\partial T}\right)_p-v\right)$. There is thus a fall in temperature on expansion when this quantity is negative and a rise when it is positive, while there will be no change in temperature on expansion when $\left(\frac{\partial v}{\partial T}\right)_p=\frac{v}{T}$. Points satisfying this condition lie on what is known as the "inversion curve" and when plotted on a **p.t.** (reduced pressure and temperature) diagram are found to give a parabola or some similar curve according to the equation of state adopted. Points lying inside the curve represent conditions which lead to cooling on expansion, points outside the curve to warming on expansion.

In any actual liquefier the pressure drop is finite and usually large (150 atm. to 1 atm.) and the drop in temperature ΔT is produced by the "integral Joule-Thomson effect":—

$$\Delta T=\int_{p_A}^{p_B}\frac{T^2}{C_p}\frac{\partial}{\partial T}\left(\frac{v}{T}\right)\,.\,dp.$$

The "integral effect" also inverts for certain conditions of p and T and gives an "inversion curve" similar to that of the "differential effect."

In applying the Joule-Thomson effect to the liquefaction of gases it is first necessary so to choose the initial pressure and temperature of the gas that expansion produces a fall in temperature throughout the range of temperature which will exist in the liquefier. This condition presents no difficulty with air, as the effect is negative at room temperature for any pressure likely to be employed. On the other hand, the effect is positive at room temperature with hydrogen and helium. In actual practice these gases are cooled to 65°-90° K. and 15° K. respectively before expansion in order to bring them well inside the "inversion curve."

The temperature at which the gas enters the actual liquefier having then been fixed, we can enquire what pressure of the gas before expansion will give a maximum yield of liquid. This can be calculated as follows :—

Suppose the liquefier has reached a steady state and is liquefying gas at a constant rate. A certain quantity of gas enters the apparatus per second at a pressure p_A and temperature T_A. The gas expands to a pressure p_B and a certain fraction ϵ is liquefied and collects at the bottom of the liquefier at temperature T_C. The remainder passes through the heat interchanger and leaves at a pressure p_B and temperature T_B. If the interchanger is perfect, $T_B = T_A$. When the steady state has been reached we can equate the "total heat" of the compressed gas entering the liquefier to the sum of the "total heat" of the liquid produced and that of the expanded gas leaving the apparatus. Or if H_A, H_B, H_C are the total heats per unit mass, we have

$$H_A = (1 - \epsilon)H_B + \epsilon H_C$$

$$\epsilon = \frac{H_B - H_A}{H_B - H_C}. \quad . \quad . \quad . \quad (3)$$

The fraction ϵ is known as the efficiency of the liquefier. We have to determine the conditions for which ϵ is a maximum. Since now p_B, T_B, p_C, T_C and T_A are all fixed by the design of the liquefier, the yield can be varied only by varying p_A, the input pressure. From the above formula ϵ will be a maximum when H_A is a minimum (H_B and H_C are constant). This occurs when $\left(\frac{\partial H_A}{\partial p}\right)_T = 0$. Now from equation (2) the change in temperature produced by the differential Joule-Thomson effect is given by

$$dT = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T . dp.$$

Hence the above condition for a maximum yield of liquid requires that the input pressure and temperature are situated on the inversion curve of the differential Joule-Thomson effect.[1] A knowledge of the inversion curve therefore permits the calculation of the most favourable input pressure for any chosen input temperature and the theoretical efficiency can be deduced when H is known as a function of p and T.

Thus for air Hausen's [2] data for the Joule-Thomson effect show that the maximum efficiency is obtained when the input pressure is 275 atm. if the air enters at room temperature (290° K.) and expands to 1 atm. pressure. This may be compared with the conditions employed in the Hampson * liquefier, input pressure 150-200 atm., input temperature 290° K., expansion to 1 atm. This liquefier does not, therefore, work under the theoretically most favourable conditions. It has, however, the advantage of simplicity and ease of manipulation and is used for the small scale production of liquid air for laboratory purposes. The theoretical efficiency for the actual input conditions is such that about 8 per cent. of the air entering the liquefier should be drawn off as liquid. Actually the efficiency of the commonly used 1 litre/hour size machine is rather less than that.

In the larger air liquefiers using the Linde process the overall efficiency is increased by two differences in technique compared with the Hampson process. The air enters the liquefier at 200 atm. pressure after being cooled to about $-40°$ C. by means of an ammonia refrigerating machine, whereby the fraction of air liquefied is considerably increased. Further, the air expands to about 40 atm. instead of to 1 atm., whereby the Joule-Thomson cooling is not greatly reduced but the amount of work which has to be done in compressing

---

* It is assumed that the reader is familiar with the constructional details of the Hampson and Linde air liquefiers. Diagrams illustrating the processes are to be found in most advanced text-books on Heat.

the air is much less. The main bulk of the air has only to be compressed from 40 to 200 atm., and only that fraction of the air which actually liquefies and so leaves the circulation has to be compressed from 1 atm. to 200 atm. Since the work done in compressing a gas isothermally from pressure p_1 to pressure p_2 is RT log $\frac{p_1}{p_2}$, it will be seen that there is a considerable saving in power required by adopting Linde's procedure. Thus 2·7 kilowatt-hours are theoretically required to produce 1 kilogram of liquid air by simple expansion from 290° K. and 200 atm. to 1 atm., while only 0·9 kw.h. are required if the air is precooled and expanded as in the Linde process. The theoretically most favourable input pressure for an input temperature of − 40° C. and expansion to about 40 atm. is 210 atm. in agreement with the figure (200 atm.) actually used.

Similarly one can calculate that the optimum input pressure for the liquefaction of hydrogen is about 160 atm. when the input temperature is between 63° and 80° K. and the gas expands to 1 atm. Actually pressures from 150 to 165 atm. are found to give the greatest yield of liquid and the actual efficiency obtained is very close to that calculated theoretically (0·285 in place of 0·295 for the Leiden liquefier with $p_A = 150$ atm., $T_A = 63°$ K.). For helium the optimum input pressure is about 30 atm., for an input temperature of 15° K. and expansion to 1 atm. Actually this pressure gives the best results in practice and a yield of about 0·13 is obtained.

The problem of the liquefaction of hydrogen is more complicated than that of air. The compressed gas has to be cooled as far as is readily possible below the inversion temperature before being allowed to expand, some means has to be adopted to prevent the narrow tubes of the liquefier being blocked by the freezing of the traces of impurity present in commercial hydrogen (mainly oxygen) and special precautions have to be taken to eliminate the risk of explosion (a 5 per cent. hydrogen-air mixture is violently explosive).

The liquefaction of hydrogen was first achieved by Dewar in 1898. Since then a number of small and large scale plants have been erected for this purpose in various parts of the world, the best known being that at the Kamerlingh Onnes Laboratory of the University of Leiden, Holland (25 litres per hr.) and that at the Physikalisch-Technische Reichsanstalt in Berlin (15 litres per hr.) *

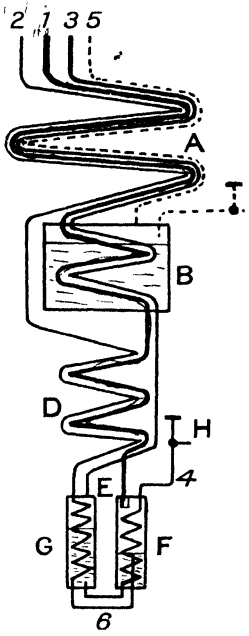

FIG. 2.

Fig 2 shows diagrammatically the construction of the hydrogen liquefier of the Mond laboratory of the Royal Society at Cambridge.[3] A limited quantity of very pure hydrogen is compressed to 160-170 atm. and enters the liquefier at 1. It passes through the interchanger A (actually a series of fine tubes in parallel) and then through the cooling bath B, where it is cooled to about 66° K. in liquid nitrogen boiling under reduced pressure. It next passes through the regenerator coil D, expands to 1 atm. at the valve E and partially liquefies into the container F. When F is about one-third full the liquid hydrogen passes through the tube 6 and the coil in the interchanger G. It evaporates there and passes back through the coils D and A and leaves

---

* For a description of the liquefiers and the precautions taken for safety see Leiden Comm. No. 158 and Suppl. No. 45 (Leiden liquefier) and Geiger-Scheel, "Handbuch der Physik," vol. 11, article by Meissner, and Wein-Harms, "Handbuch der Experimental Physik," vol. 9, Part I, article by Lenz (Berlin liquefier).

the liquefier at 2. The hydrogen is then recompressed and returns to the apparatus again. The compressed gas is thus cooled progressively in A, B and D until the temperature falls low enough on expansion for part of the gas to liquefy in F. The heat interchange is so efficient that the expanded gas leaves at 2 at only a few degrees below room temperature. Ordinary commercial hydrogen from cylinders enters the liquefier at 3 at a pressure of 3-4 atm. It is cooled in the interchanger A and the nitrogen bath B and then passes into G. It there meets the spiral cooled with liquid hydrogen and liquefies on it at the pressure of 3 atm. The liquid hydrogen produced in the chamber G passes through the spiral in F, where its temperature falls to that of liquid hydrogen boiling under 1 atm. pressure, 20° K., and is finally drawn off at the valve H into a suitable container. The impurities present in the commercial hydrogen solidify in G and not before and, as they are denser than liquid hydrogen, they collect at the bottom of G and can be removed at the end of the run. The whole liquefier is enclosed in a metal case in which a high vacuum is maintained so as to provide good heat insulation.

The liquefier in its present form receives compressed hydrogen at the rate of 16 c. metres per hr. and produces about 4 litres of liquid per hr. The efficiency (about 0·25) is in good agreement with that calculated from expression (3) for the input conditions employed.

The liquefaction of helium is a matter of still greater difficulty than that of hydrogen, as the gas must be cooled in liquid hydrogen before the Joule-Thomson effect can be used to lower the temperature below the critical temperature (5·2° K.). Helium was first liquefied by Kamerlingh Onnes at Leiden in 1908 and until recent years this was the only place in the world at which physical measurements could be made in the range of temperature 1·5° to 4·2° K. Several relatively large scale helium liquefiers (yield 1-2 litres per hr.) are however now in existence and reference may be made to the papers cited in the footnote on page 7 for the details of the plant at Leiden and Berlin. Fig 3 shows the small scale helium liquefier designed by Ruhemann,[4] which has the merit of extreme simplicity. Helium from a cylinder passes through a reducing valve, then through a tube containing charcoal immersed in liquid air to remove impurities, and enters the liquefier at O at a pressure of 30-40 atm. It then traverses the coil L in the bath of liquid hydrogen in the Dewar vessel G and so is cooled well below the inversion temperature which lies below the temperatures obtainable with liquid air. The gas then passes through the inner tube R_1 of the Linde pattern interchanger A which is enclosed in the evacuated metal case M. It then expands to 1 atm. pressure at the valve D (not shown in detail) and after passing through the outer tube R_2 of the interchanger escapes into the atmosphere at P. With a rate of flow of about 1·5 litres per min. and the liquid hydrogen boiling at about 10 cms. pressure (T = 15° K.) the receiver B is cooled to the temperature of the normal boiling-point of helium, 4·2° K., in 7 mins. The amount of liquid hydrogen required is quite small, about 1·5 litres. The temperature of B is indicated by the small gas thermometer C, the metal bulb of which is directly attached to the bottom of B. C is connected to a mercury manometer by means of the fine capillary R_5.

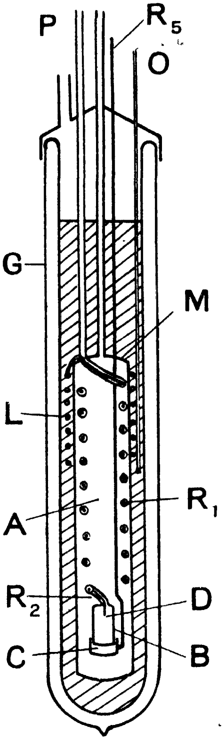

Fig. 3.

This small liquefier permits of experiments being made at temperatures from 15° K. down to about 1·9° K.

with any apparatus or material which can be enclosed in the receiver B and at relatively small cost.

THE "EXTERNAL WORK" METHODS OF GAS LIQUEFACTION

Suppose a volume of gas v_1 enters the cylinder of an engine at a pressure p_1 and then expands adiabatically and reversibly, forcing down the piston (supposed frictionless) and doing work on some external system until the volume has increased to v_2 and the pressure has fallen to p_2. The outlet valve then opens and the piston rises, forcing the gas out at pressure p_2. Then the total amount of work done by the gas will be

$$\int_2^1 v dp = H_1 - H_2$$

and the temperature of the gas will fall from T_1 to T_2. If the equation of state of the gas can be written as $pv = (C_p - C_v)T$ (C_p, C_v specific heat at constant pressure and volume respectively), the work done will be

$$W = C_p(T_1 - T_2) = H_1 - H_2$$

and the final temperature will be given by

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{\frac{C_p - C_v}{C_p}}. \quad . \quad . \quad (4)$$

The drop in temperature calculated from (4) is greater than that obtained by throttle expansion from pressure p_1 to pressure p_2. It would thus seem that it is preferable to cool the gas by the performance of "external" work rather than "internal" work in the liquefaction of gases. In actual practice the difficulties of the realization of the "external" work method make the two types of process of practically equal efficiency for air liquefaction.

The application of the expansion engine to the liquefaction of gases forms the basis of the Claude and Heylandt methods. Fig. 4 illustrates one of the types of liquefier employing the Claude process. Air compressed to about 40 atm. passes through the interchanger I, where it is cooled to about – 80° C. by the expanded gas. It then divides, a fraction M passing through the interchanger II and 1 – M through the expansion engine E. The gas expands in the engine to 1 atm. pressure (in some Claude liquefiers in two stages 40-6·3 and 6·3-1 atm.), doing external work such as driving a dynamo and is cooled thereby. The cold gas then passes through the interchanger II and so cools the fraction M of the gas that a portion of it liquefies and collects in L after expansion to 1 atm. pressure at the valve V. The portion which is not liquefied returns to the open air through the interchangers III, II and I as shown. The expansion engine is not used to lower the temperature of the air to such an extent that it liquefies in the cylinder but only to produce part of the necessary cooling, the remainder being obtained by throttle expansion at V. This is done for technical reasons mainly, because of the in-

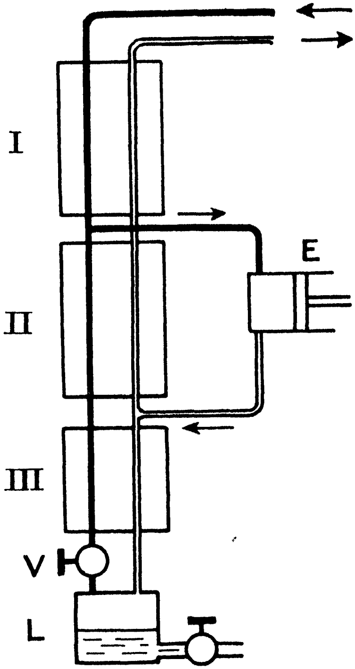

FIG. 4.

creasing difficulty of lubricating the piston at low temperatures.

The efficiency of the liquefier depends in a rather complicated way on the temperature and pressure of the air before expansion in the engine and the fraction $1 - M$ of the air passing through it. For each initial pressure there is a most favourable value of the temperature of the air before expansion in E for every value of M and the actual conditions are best determined by experiment. Typical figures are: pressure = 40 atm., $M = 0{\cdot}2$ (i.e. 20 per cent. of the air goes through the throttle and 80 per cent. through the expansion engine) and $T_2 = -80^\circ$ C.

The Heylandt process differs from the Claude process in detail rather than in principle. In this case the air is compressed to 200 atm. and a fraction $1 - M$ enters the expansion engine at room temperature. After expansion the cold air passes through an interchanger, cooling the fraction M of the compressed air which is then allowed to expand to 1 atm. at a valve and partially liquefies.

One of the principal technical difficulties in the application of the "external work" method is that of maintaining the piston of the expansion engine gas-tight and lubricated in spite of the low temperature of the expanded air. The cylinder of the Claude engine is heat insulated and so reaches a temperature approximating to that of the expanded air and the piston is maintained gas-tight by means of a patented impregnated leather cup which needs no further lubrication. The Heylandt engine is not insulated and remains approximately at room temperature so that ordinary lubrication can be employed. It is, however, run at high speed, so that the expanded air is swept out of the cylinder before it can cool the latter appreciably.

The Claude process, using a pressure of 40 atm. and with a partition ratio $M = 0{\cdot}2$, requires 0·87 kilowatt-hr. per kilogram of liquid air produced, thus nearly the same as the Linde process. The Heylandt process, using a pressure of 200 atm. and M = 0·4, requires about 0·7 kilowatt-hr. per kilogram of liquid air.

The "external work" method has not been applied successfully to the liquefaction of hydrogen or helium and it is not probable that it will prove advantageous to do so.* While the fall in temperature on throttle expansion increases with decreasing initial temperature, that produced by the expansion engine decreases with decreasing initial temperature since in the latter case the ratio of the initial and final temperatures remains the same for any given ratio of initial and final pressures.

Simon's Desorption Method

A further method by which very low temperatures can be produced and if desired helium liquefied on a small laboratory scale deserves mention. The method was suggested by Simon [5] and is illustrated schematically in Fig. 5. Charcoal C which has been previously activated and freed from gas is cooled to the temperature of the bath of liquid hydrogen contained in the vacuum vessel by conduction across the space *f*. Helium is then allowed to enter through the taps 1 and 2 and is adsorbed in relatively large quantities by the cold charcoal. The space *f* is then evacuated so as to insulate the charcoal and the adsorbed helium

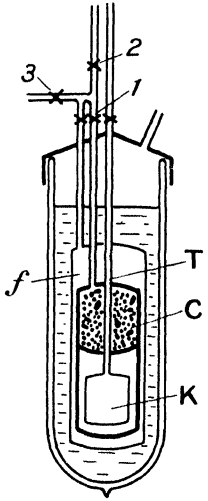

Fig. 5.

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* Since the above was written Kapitza has, however, succeeded in liquefying helium by firstly cooling the compressed gas to about 66° K. in a bath of liquid nitrogen, then to about 9° K. in a specially designed expansion engine which ingeniously avoids lubrication difficulties and which apparently works regeneratively (the Claude and Heylandt engines are non-regenerative), and finally to 4° K. by Joule-Thomson cooling at an expansion valve.

is pumped off through the taps 1 and 3. The heat of adsorption of the helium on the charcoal is removed and the temperature of the latter falls to such an extent (below 5·2°, the critical temperature) that if helium at a suitable pressure is passed through the tube T it condenses and collects in K. The experimental apparatus, such as a calorimeter, can be enclosed in K and so measurements made between 14° K., the lowest temperature obtainable with the liquid hydrogen bath, and about 2° K. The method permits of "helium temperatures"* being obtained at relatively small cost, provided liquid hydrogen is available. For some purposes the apparatus can be immersed directly in the charcoal and the liquefaction of the helium dispensed with, so further reducing the cost of the experiment.

The same principle can be employed to produce temperatures below the lowest obtainable with liquid air by the adsorption of hydrogen, using liquid nitrogen as the cooling bath. It is also possible to liquefy hydrogen in small quantities with the aid of this apparatus.

THE MANIPULATION OF LIQUEFIED GASES AND THE MAINTENANCE OF LOW TEMPERATURES

Liquefied gases can be stored in the now familiar vacuum vessels (or Dewar vessels) of glass or metal with relatively little loss by evaporation. A typical metal vacuum flask is shown in Fig. 6. The charcoal C serves to adsorb the residual gases in the vacuum space when cooled by the liquefied gas and so maintain an adequately high vacuum. The long narrow neck of nickel-silver minimizes loss by conduction. Such vessels will preserve liquid air for many days, the loss with a good 15-litre flask being about 7 per cent. of the contents per day.

Liquid hydrogen can also be stored in glass or metal vacuum flasks, the metal ones for this purpose being provided with a radiation shield or a third surface, cooled with liquid air, in the vacuum space between the inner and outer walls. Although the latent heat per gram of liquid hydrogen is not very different from that of liquid oxygen, the volume of hydrogen lost by evaporation per unit time for any flask will be much greater than the volume of oxygen lost on account of the remarkably low density of liquid hydrogen (0·08 at 20° K against 1·13 at 90° K. for liquid oxygen). On account of its very great volatility liquid helium is not usually stored and transported but the experiments are generally made in the liquefier itself or in a vessel directly attachable to the latter.

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* It is convenient to speak of "helium" or "hydrogen" temperatures when the temperatures obtainable with these liquefied gases are intended.

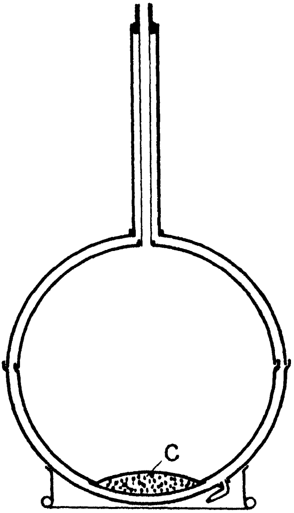

FIG. 6.

In the case of liquid hydrogen and helium it is essential to prevent air coming into contact with the liquid as otherwise the flask would rapidly fill with solidified air. The flask is therefore closed with a metal cap provided with an inlet and outlet for the liquid and an outlet for the vapour produced by the evaporation of the liquid. The liquid is then transferred to any apparatus to be filled by blowing it over with an excess pressure of the same gas from a cylinder with a reducing valve or from a rubber balloon in which the vapour has been allowed to collect by temporarily closing the vapour exit. The connection between the supply flask and the apparatus is best made with a tube which is itself silvered and vacuum-jacketed to present loss by evaporation.

Liquefied gases can be applied in various ways to the maintenance of low temperatures. In one type of cryostat (or low temperature thermostat) a bath of some liquid which does not solidify at the low temperatures required is cooled by means of liquid air and the temperature adjusted if necessary by means of the current in the heating coil. Thus in the Henning cryostat,[6] Fig. 7, pentane contained in a vacuum vessel is cooled by a slow stream of liquid air through the porcelain U-tube G. A stirrer keeps the pentane in motion and serves to maintain a uniform temperature. The temperature of the bath is determined by the rate of flow of the liquid air into G and can be kept constant to a few hundredths of a degree over the range 0° to – 150° C. Other cryostats of this type differ in the mode of application of the liquid air to the cooling of the pentane bath. The disadvantage of these cryostats is the danger of explosion of the very inflammable pentane, but this can be avoided for the higher temperatures 0° to – 81° C. by the use of a non-inflammable mixture of carbon tetrachloride and chloroform.

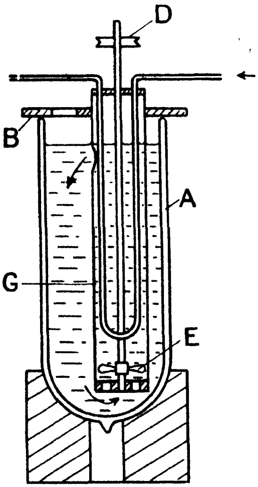

Fig. 7.

A further type of cryostat employs a regulated stream of cooled gas as the refrigerating agent. Thus hydrogen may be passed through a bath of liquid air into the vacuum vessel containing the experimental apparatus, using an arrangement similar to that of Fig. 9, and temperatures down to – 180° C. maintained constant. The chief limitation of such a cryostat is the small heat capacity of the gas.

The most highly developed method of obtaining accurately controlled low temperatures is that of immersing the apparatus directly in a bath of some pure liquefied gas. The liquid is stirred and the pressure at which it is boiling is accurately controlled. The pressure range usually employed is that from atmospheric pressure downwards so that any temperature from the ordinary boiling-point to the triple-point can be obtained. For this purpose the vacuum vessel containing the liquid is closed by some suitable cap to exclude air and to enable the pressure to be reduced. The vapour from the evaporating liquid passes either direct to a gas-holder (or the outer air) or through a needle-valve and a vacuum pump to the gas-holder. When the desired pressure has been reached it can be maintained constant by manipulating the needle-valve in accordance with the indications of a sensitive oil-manometer. With adequate stirring the temperature can be obtained with sufficient accuracy for many purposes from the reading of the manometer, using the known data for the vapour pressure-temperature curve.

The most commonly employed liquefied gases * are contained in Table I together with their boiling-points and triple-points. In the absence of special facilities for the purpose any of these gases from methyl chloride to nitrogen can be liquefied when required with the aid of liquid air (see Table 1).

It will be seen that the range of temperature from − 24° to − 218° can be completely covered. There are, however, gaps between oxygen and hydrogen (− 218° to − 253°) and between hydrogen and helium (− 259° to − 269°) which cannot be completely bridged by any liquid or liquids.

Fig. 8 illustrates the employment of this method to

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* Solid carbon dioxide, either dry or mixed with alcohol, ether or acetone, is often used as a refrigerating agent, giving a temperature of − 78·5° C. The constancy of the temperature of apparatus immersed in such a cooling agent is not, however, as good as with a liquefied gas.

TABLE 1.

Substance.	Boiling-point.	Triple-point.	Triple-point Pressure.
Methyl chloride .	− 24·1°	−103·6°	—
Nitrous oxide .	− 89·8°	−102·4°	—
Ethylene . .	−103·7°	−169·0°	—
Methane . .	−161·4°	−183·1°	7 cm.
Oxygen . .	−182·9°	−218·4°	0·2 cm.
Nitrogen . .	−195·8°	−209·9°	9·6 cm.
Hydrogen . .	−252·76°	−259·14°	5·07 cm.
Helium . .	−268·83°	—	—

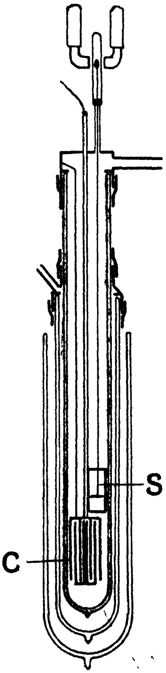

FIG. 8.

the determination of the dielectric constant of liquid helium (Keesom and Wolfke). The experimental condenser C is immersed in the bath of liquid helium contained in the innermost vacuum vessel. The liquid is stirred by the magnetically operated stirrer S and is surrounded by baths of liquid hydrogen and liquid air to reduce the heat entry as much as possible. The helium and hydrogen vessels are closed at the top as shown.

The gap between − 218° and − 253° has been bridged by Kamerlingh Onnes and Crommelin [7] by means of a hydrogen vapour cryostat shown diagrammatically in Fig. 9. Hydrogen from a cylinder passes through the coil C immersed in liquid hydrogen in the vacuum vessel I and is cooled to about 20° K. It then passes through a vacuum-jacketed tube into the vacuum vessel II, where it encounters an electrical heater E. Its temperature is there raised to that at which the experimental apparatus in II has to be maintained. The rate of flow of the gas can be adjusted to the desired value and with automatic regulation of the heating current supplemented if required by hand regulation by an observer watching the galvanometer in the circuit of a resistance thermometer in II a constancy of 0·01° can be obtained.

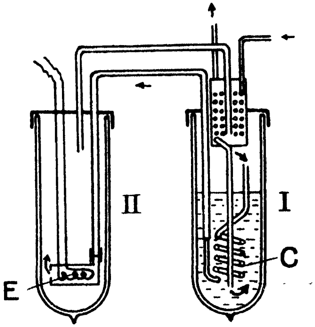

FIG. 9.

The gap − 259° to − 269° could be similarly bridged by means of a helium vapour cryostat. It is also possible to reach 9° K. with solid hydrogen. When the pressure above liquid hydrogen is reduced below 5 cm. the hydrogen solidifies and by further reducing the pressure the temperature of the solid can be reduced to as low as 9° K. For certain purposes it is possible to employ solid hydrogen as the cooling agent.

THE PRODUCTION OF TEMPERATURES BELOW 1° K.

Since the lowest pressure which can be readily maintained over liquid helium with the aid of mechanical pumps is about 0·5 mm., the temperature to which this pressure corresponds, 1·2° K., is the lowest at which it is generally possible to carry out physical experiments in the various cryogenic laboratories. Temperatures lower than 1·2° K. have been obtained by the use of special apparatus and methods.

In 1921 Kamerlingh Onnes[8] attempted to reduce the pressure over liquid helium as far as possible in order to determine whether helium can be solidified in this way. A small vacuum vessel containing a few cm.^{3} of liquid helium was immersed in liquid helium boiling under low pressure and precautions were taken to cut down the entry of heat into the inner vessel as much as possible. The pressure over the liquid helium was then lowered by means of a battery of 18 diffusion pumps backed by a mechanical pump. The lowest pressure recorded was 0·013 mm. and the temperature was estimated to be 0·82° K. At this temperature, however, the helium still remained a mobile liquid.

Keesom [9] in 1932 repeated this experiment with improved equipment. Two specially designed diffusion pumps gave a pumping speed of 675 litres per sec. compared with the 80 litres per sec. of Onnes' pumping system. The lowest pressure, measured immediately above the surface of the liquid helium, was 0·0036 mm. This corresponds to a temperature of 0·71° K. (see Chapter II). The helium was still liquid and gave no indication that a further lowering of the temperature by this method would lead to its solidification. An explanation of this behaviour was found when solid helium had been obtained by another method.

It will be seen that there is very little prospect of further progress towards the Absolute Zero along these lines even with very elaborate and costly equipment.

The same pumping system has, however, been used by Keesom to build a cryostat in which a space of about 300 cm.^{3} can be cooled to 0·9° K., thereby making it possible to carry out many different kinds of physical investigations down to this temperature.

Recently, however, it has been shown that temperatures below 1° K. can be obtained by two other methods. The method suggested by Debye [10] and by Giauque [11] consists in magnetizing a paramagnetic solid substance at as low a temperature as possible, say 1·3° K., conducting away the heat produced in the process, then thermally insulating the solid and finally switching off the magnet. The field and consequently the magnetization of the solid falls to zero or some low value and as no heat enters from outside this stage of the process takes place adiabatically. If dU is the change in the internal energy of the paramagnetic solid when a quantity of heat dQ is added to it and its magnetization is changed by an amount $d\sigma$ when a magnetic field H is applied, then we have

$$dU = dQ + Hd\sigma = Td\phi + Hd\sigma$$
$$(\phi = \text{entropy}).$$

Now since the magnetization is a function of H/T only and U of T only, it follows that the entropy ϕ can be considered to be made up of two parts, ϕ_1 and ϕ_2, which are of a thermal and a magnetic nature respectively.

$$\phi_1 = \int \frac{1}{T}\frac{dU}{dT} \cdot dT \quad \text{(thermal)},$$
$$\phi_2 = -\int \frac{H}{T} d\sigma \quad \text{(magnetic)}.$$

If we write $x = H/T$ and $\sigma = f(x)$,

$$\phi_2 = -\int x f'(x) dx. \quad . \quad . \quad . \quad (5)$$

If now the magnetization is decreased adiabatically to zero, then since $\phi_1 + \phi_2$ must remain constant, ϕ_1 must decrease to compensate the increase in ϕ_2. Thus adiabatic demagnetization will result in a fall in the temperature of the solid and to an extent which is calculable when $f(x)$ and the specific heat of the paramagnetic substance is known.

Taking the data of Kamerlingh Onnes and Woltjer [12] on the magnetization of gadolinium sulphate down to 1·3° K. (see Chapter VI) and extrapolating the specific heat of this substance by the Debye T^3 law (Chapter IV) from the lowest temperature at which it had then been measured (15·4°), Giauque and Clarke [13] calculated the fall in temperature to be expected for various initial temperatures and field strengths. The results showed that temperatures in the neighbourhood of 0·2° K. should be readily obtained. It has, however, since been found that the specific heat of $Gd_2(SO_4)_3 \cdot 8H_2O$, instead of falling off as T^3, shows a very pronounced maximum at about 0·27° K.[14, 15] It is thus not an ideal substance for the purpose in view, as the cooling obtained with a given magnetic field is much reduced by this anomaly in the specific heat. Giauque and MacDougall,[16] using this substance and with a magnetic field of 8000 gauss, have, however, succeeded in reaching a temperature of 0·25° K.

Almost simultaneously de Haas, Kramers and Wiersma[17] announced that they had obtained a temperature of 0·27° K. by the adiabatic demagnetization of cerium fluoride. Cerium salts do not show an anomalous specific heat in the region in question and the last mentioned workers have succeeded in lowering the temperature of cerium ethylsulphate to 0·085° K. and more recently that of potassium chromium alum to 0·05° K. *The latter is the lowest temperature yet obtained.*

The temperatures in these experiments were deduced from the observed susceptibilities of the paramagnetic substance, using the formulæ connecting susceptibility and temperature which have been established for higher temperatures. This, of course, involves an extrapolation, but there is no reason to doubt that the temperatures reached were at least as low as stated.

A further method of obtaining temperatures below 1° K. has recently been suggested by Simon.[18] He proposes to make use of the cooling produced by allowing a fluid to expand reversibly and adiabatically with the performance of external work (as in the Claude process), using liquid helium as the working substance. As liquid helium has the greatest compressibility of any known liquid an appreciable cooling is to be expected for a quite moderate initial pressure. This latter has in any case to be less than about 25 atm., as helium solidifies under this pressure at any temperature below 1·3° K. By making the method regenerative any arbitrarily low temperature could theoretically be reached by this method.

Meissner,[19] who was working independently on the same idea, has, however, shown that it is necessary to *compress* the liquid helium to *cool* it from any initial temperature below 2·19° K. The cooling effect for such a process is determined by the relation

$$\left(\frac{\partial T}{\partial p}\right)_\phi = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p,$$

and $\left(\frac{\partial v}{\partial T}\right)_p$ is negative for temperatures below 2·19° K. (see Chapter III). It is difficult to predict what may be the lowest temperature obtainable in practice, but the method is likely to be limited by the fact that $\left(\frac{\partial v}{\partial T}\right)_s$ (rate of change of volume with temperature at the saturation vapour pressure) and apparently also $\left(\frac{\partial v}{\partial T}\right)_p$ becomes progressively numerically less as the temperature decreases. If the mechanical difficulties of the process can be overcome, the method will enable temperatures well below 1° K. to be obtained with much less costly and elaborate equipment than is necessary with the adiabatic demagnetization method.

The new methods will make a new temperature region available for investigation and results of great interest and importance may confidently be expected when physical measurements have been made in this domain. Thus the mechanical and magnetic properties of the nuclei of atoms will be of paramount importance at temperatures of the order of 0·01° K.

CHAPTER II

THE MEASUREMENT OF LOW TEMPERATURES

THE measurement of any low temperature in an experiment is almost invariably carried out with the aid of some suitable secondary thermometer. The determination therefore involves two processes, the actual measurement of the low temperature and the calibration of the thermometer. For this calibration the temperature of certain " fixed points " must have previously been determined with the aid of a standard instrument, preferably on the thermodynamic scale.

Standard measurements of low temperatures are made almost exclusively with the constant volume gas thermometer, generally filled to a pressure of 1000 mm. Hg. at 0° C. with hydrogen or helium. The temperature scale so obtained is known as the normal hydrogen (or helium) scale.

The temperatures are deduced from the observed pressure of the gas in the thermometer from the relation

$$t_v = \frac{p_{t_v} - p_0}{p_{100} - p_0} \times 100,$$

or

$$p_{t_v} = p_0(1 + \alpha t) = p_0 \alpha T_v,$$

in which p_{t_v}, p_{100}, p_0 are the pressures at t_v, 100° and 0° C.,

α = coefficient of increase of pressure with temperature,
t_v = centigrade temperature,
T_v = absolute temperature.

The observed pressure must be corrected for the thermal expansion of the bulb of the thermometer, for the change in volume of the bulb with internal pressure, for the fact that the "dead space" (the volume enclosed between the fixed meniscus of the mercury in the manometer and the actual bulb of the thermometer) is not at the temperature to be measured and for the variation of the dead space with temperature. The normal hydrogen scale so obtained can be employed down to – 250° C. and the helium scale down to –270° C.

For the measurement of "helium temperatures," say 4·2° K. to 0·9° K., with the gas thermometer the zero-point pressure must be chosen much smaller than 1000 mm. and helium at pressures from 10 cm. to 0·2 cm. is used. The pressures observed at helium temperatures are then so small that the mercury manometer usually employed is replaced by a Pirani or hot wire manometer, in which the pressure is deduced from the resistance of a fine wire exposed to the gas. The main uncertainty in the measurement of these very low temperatures lies in the fact that a correction has to be applied for the thermal molecular difference of pressure. When two bulbs, containing gas at such a low pressure that the mean free path of the molecules is comparable or large compared with the diameter of the connecting tube, are at different temperatures there is a difference in pressure between them known as the thermal molecular pressure. Since a complete theoretical treatment of this effect is not yet available there is some uncertainty in the value of the correction to be applied in the thermometry of very low temperatures to allow for the fact that the bulb is at the low temperature and the hot wire manometer at 0° C. Different thermometers after the correction has been applied agree, however, to within about 0·01°.

The readings of the gas thermometer can be corrected so as to give absolute or thermodynamic temperatures, provided the equation of state of the thermometric gas is sufficiently well known. Thus it can be shown that a gas thermometer containing a "perfect gas," i.e. a gas obeying the law $pv = R\theta$, would give readings directly on Kelvin's thermodynamic scale of temperature. It is also known that any real gas approaches the perfect gas in its properties more closely the lower the pressure. If then the readings of any real gas thermometer are extrapolated to the limit of vanishingly small pressure, the scale so obtained will agree with the perfect gas scale. This extrapolation can be carried out as follows :—

The equation of state of any real gas can be written in the form

$$pv = A + Bp + Cp^2 + \dots \quad (1)$$

or

$$pv = A + B/v + C/v^2 + \dots \quad (2)$$

in which A, B and C are functions of the temperature. In expression (1) if the unit of pressure is 1 metre of mercury, then B/A is of the order 10^{-3} and C/A 10^{-5} to 10^{-6}.

Taking expression (1) and neglecting the terms involving C, we can write for the case of the constant volume thermometer at temperatures t, 100° and 0°,

$$\begin{aligned} p_0v_0 &= A_0 + B_0p_0, \\ p_{100}v_0 &= A_{100} + B_{100}p_{100}, \\ p_tv_0 &= A_t + B_tp_t. \end{aligned}$$

The gas scale temperature t_v is given by

$$t_v = 100 \cdot \frac{p_{t_v} - p_0}{p_{100} - p_0} = 100\left\{\frac{A_t - A_0 + B_tp_t - B_0p_0}{A_{100} - A_0 + B_{100}p_{100} - B_0p_0}\right\}$$

and the corresponding temperature for the limit $p \rightarrow 0$ is obviously

$$t(\lim) = 100 \cdot \frac{A_t - A_0}{A_{100} - A_0}$$

since the gas in the limiting case $p \rightarrow 0$ follows the law $pv = A$. The difference between t_v and $t(\lim)$ is then the correction to be applied to t_v to extrapolate to $p \rightarrow 0$.

Subtracting the two expressions above, expanding by the Binomial Theorem and neglecting terms in $(Bp_0/A)^2$ we obtain

$$t(\text{lim}) - t_v = t(\text{lim})\left\{\frac{B_{100}p_{100} - B_0p_0}{A_{100} - A_0} - \frac{B_tp_t - B_0p_0}{A_t - A_0}\right\}.$$

Thus provided the values of A and B are known from determinations of the isotherms of the thermometric gas, we can calculate the corrections to be applied to the readings of any gas thermometer to convert them into thermodynamic temperatures. It will be seen that the correction itself contains $t(\text{lim})$ as written above. In using the formula the uncorrected value t_v is first inserted and a value of the correction obtained. This correction is then applied and the corrected value of t inserted in the formula, so deriving a second approximation to the value of the correction.

It has been found that the scales of all gas thermometers corrected in the above way agree with each other to within about the accuracy claimed for the measurements and with the thermodynamic scale obtained in other ways, for example, from observations on the Joule-Thomson effect.*

The magnitude of the corrections may be judged from the values given in Table 2 for the constant volume H_2 and He thermometers with a zero-point pressure of 1000 mm. Hg derived from the measurements of Holborn and Otto [1] and of Onnes and Cath.[2]

TABLE 2

t (°C.).	H_2.	He.
0	0·00	+0·00
− 50	+0·006	+0·003
−100	+0·015	+0·008
−150	+0·027	+0·014
−200	+0·069	+0·020
−250	+0·135	+0·037

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* For a description of the method of correcting the gas thermometer to the thermodynamic scale with the aid of the Joule-Thomson effect see, for example, Roberts, "Heat and Thermodynamics," p. 256.

The corrections to be applied in the temperature range 4·2° K. to 0·9° K., when the zero-point pressure is 10 cms. or less, are smaller than the errors of observation and can be neglected.

For the limiting case of infinitely small pressure the scales of the constant volume and constant pressure thermometers are the same and agree with that given by the expression

$$\begin{aligned}\lim_{p \to 0}(pv)_t &= \lim_{p \to 0}(pv)_0\{1 + \gamma t\} \\ &= \lim_{p \to 0}(pv)_0\gamma \mathrm{T},\end{aligned}$$

when $$\mathrm{T} = 1/\gamma + t.$$

$1/\gamma$ is then the temperature of the ice point on the thermodynamic scale. The values most recently obtained for γ (obtained by extrapolating α to the case $p \to 0$) are 0·00366107 (Leiden 1934) and 0·0036608 (Berlin 1929). These lead respectively to 273·14° K. and 273·16° K. for the thermodynamic temperature of the ice-point, in good agreement with the value 273·15° K. deduced by Roebuck from very careful determinations of the Joule-Thomson effect in air.

With the aid of the gas thermometer corrected as above the temperatures of the following thermometric fixed points have been determined for the purpose of calibrating secondary thermometers: melting-point of mercury (— 38·87° C.), the sublimation-point of solid carbon dioxide (— 78·51° C. at 1 atm. pressure), the boiling-point of oxygen (— 182·97° C. at 1 atm. pressure), the boiling-point of hydrogen (— 252·75° at 1 atm. pressure).

SECONDARY THERMOMETERS

(*a*) *Resistance thermometers.*

The platinum resistance thermometer can be employed to measure temperatures down to about — 258° C., below which it becomes insensitive. Provided it is so wound that the wire does not become strained on contracting as the temperature falls, the platinum thermometer retains its calibration sufficiently accurately even after repeated use at hydrogen temperatures.

Temperatures down to − 193° C. can be deduced from the resistance of the platinum wire by using the formula of Henning and Heuse[3] :—

$$R_t = R_0(1 + at + bt^2 + ct^4),$$

-5×10

in which R_t, R_0 are the resistances at t and 0° C. respectively and a, b and c are constants.

The values of the constants are determined by calibration at the ice-point (0° C.), the melting-point of mercury (− 38·87° C.), the sublimation-point of carbon dioxide (− 78·51° C.), and the boiling-point of oxygen (− 182·97° C.). Generally the coefficient c can be taken to be -5×10^{-12} and one of the calibration points, preferably the melting-point of mercury, omitted. The readings of different thermometers of adequately pure platinum so calibrated agree within an accuracy of about ± 0·02°.

For temperatures between − 193° and − 258° the platinum thermometer must be compared directly or indirectly with the gas thermometer at as many points as possible in the range required. No simple formula will accurately represent the variation of the resistance with temperature in this region.

Resistance thermometers of gold and lead can also be used at hydrogen temperatures with advantage. Since the electrical resistance of pure metals (apart from the occurrence of superconductivity, see Chapter V) becomes practically independent of the temperature in the region of helium temperatures, they cannot be employed as resistance thermometers in this region. However, the resistance of various alloys, such as manganin, constantan and phosphor-bronze, which is nearly independent of the temperature at higher temperatures, varies appreciably below 5° K. Thus it has been shown by Keesom and v. d. Ende[4] that an unannealed wire of phosphor-bronze exhibits a relatively large and practically linear variation of resistance with temperature from 5° K. to 1° K. and gives reproducible results. It is therefore very suitable for use as a secondary thermometer for helium temperatures.

(*b*) *Thermocouples.*

Various thermocouples can be used for the measurement of low temperatures. Thus the copper-constantan couple can be employed down to – 258° C. Nernst has published the following formula for the electromotive force of this couple for the range 100° K. to 15° K.:

$$e = 31{\cdot}32 \log (1 + T/90) + 1{\cdot}0 \times 10^7 T^4 \text{ microvolts.}$$

In the region of hydrogen temperatures the gold-silver couple, which gives practically no e.m.f. at room temperature, is more sensitive than the copper-constantan couple (Onnes and Clay). It has also been suggested by Keesom and Borelius [5] that a couple of 1 at. per cent. of Co in Au. against 1 at. per cent. of Au. in Ag should be used for the measurement of very low temperatures. This couple gives the following approximate values of the thermoelectric power (microvolts per deg.) at 0° 37, at – 180° 34, at – 220° 28, at – 250° 17 and at – 255° 14. It should still give appreciable e.m.f.'s at helium temperatures and is likely to be generally suitable for the measurement of very low temperatures, particularly as such dilute alloys are likely to retain their calibration during use.

(*c*) *Vapour pressure thermometers.*

The determination of the vapour pressure of a suitable liquid in equilibrium with its vapour provides a sensitive and convenient method for the measurement of low temperatures (Stock and Nielson, 1906). The substance, which must be gaseous at room temperature and liquid in the temperature region to be measured, is contained in a small bulb connected to a manometer.

The bulb is placed in the apparatus where the temperature is to be determined and the pressure shown by the manometer is the saturated vapour pressure corresponding to the temperature of the coldest part of the thermometer.

A formula connecting the vapour pressure and the temperature can be obtained by integrating the Clausius-Clapeyron equation, $\frac{dp}{dT} = \frac{L}{T(v_1 - v_2)}$ (p = vapour pressure, L = latent heat of vaporization, v_1, v_2 specific volumes of vapour and liquid respectively), using certain simplifying assumptions. The integration leads to a formula of the type below or to a somewhat more complicated expression :—

$$\log p = -a/T + b \log T - cT + k,$$

in which a, b, c and k are constants.

Table 3 below gives the values of the constants of some of the substances suitable for the determination of low temperatures. Following Nernst b is taken as 1·75 and the unit of pressure is 1 metre of mercury.

TABLE 3.

Substance.	Range °C.	a.	$c \times 10^3$.	k.
CS_2 . .	+ 12 to − 25	1682·38	5·2980	5·44706
NH_3 . .	− 35 to − 80	1393·60	5·7034	5·89437
HCl . .	− 87 to −118	905·53	5·0077	4·65491
C_2H_4 .	−110 to −141	834·13	8·3753	5·32089
CH_4 . .	−162 to −170	472·47	9·6351	4·59825
O_2 . .	−183 to −205	379·95	9·6219	4·53939

The sensitivity of the vapour pressure thermometer is much greater than that of the gas thermometer ; thus the vapour pressure of oxygen near its normal boiling-point changes by about 80 mm. Hg per deg., while with a constant volume gas thermometer with a zero-point pressure of 1000 mm. Hg the corresponding change is less than 4 mm. Hg per deg. in this temperature region.

Provided the bath of liquefied gas is adequately stirred it is frequently sufficient to determine the vapour pressure by means of a manometer attached to the exit tube of the apparatus in order to determine the temperature with an accuracy of 0·1° or somewhat better.

Temperatures obtainable with a bath of liquid hydrogen can be deduced from the formula :—

$$t = -260{\cdot}865 + 1{\cdot}0619 \log_{10} p + 1{\cdot}7233 (\log_{10} p)^2 \qquad (p \text{ in cm. Hg.}).$$

The temperatures of liquid helium baths are almost always obtained from the pressure under which the liquid is boiling and it is the general practice to give both the vapour pressure and the estimated temperature in tables of data. Earlier results can then be corrected later as the vapour pressure-temperature relation becomes better known. This latter has been the subject of much experimental work. The latest results of Keesom, Weber, Nøgaard and Schmidt,[6] which can probably be regarded as definitive to within the accuracy claimed (about 0·01°), show that the vapour pressure of liquid helium requires two formulæ to represent it as a function of the temperature, one for temperatures above 2·19° K. and one for temperatures below this. (2·19° K. is the temperature at which liquid He I changes into liquid He II under a pressure equal to the saturation vapour pressure as described in Chapter III.)

The formulæ are :

$T > 2{\cdot}19°$ K.,

$$\log_{10} p \text{ (cm.)} = -\frac{3{\cdot}024}{T} + 2{\cdot}208 \log_{10} T + 1{\cdot}217, \qquad (1)$$

$T < 2{\cdot}19°$ K.,

$$\log_{10} p \text{ (cm.)} = -\frac{\text{[illegible]}85}{T} + 0{\cdot}932 \log_{10} T + 2{\cdot}035, \qquad (2)$$

The value 0·71° K., for [illegible] lowest temperature reached by the evaporation of [illegible]id helium, is derived from formula (2) above.

(*d*) *Special cases.*

As mentioned in Chapter I the temperatures below 1° K. produced by the method of adiabatic demagnetization were estimated from a knowledge of the function $\sigma = f\left(\frac{H}{T}\right)$ at higher temperatures. It is likely that this method will be extensively developed in the near future and will become the standard method for the determination of temperatures below 1° K., particularly as the magnetization, σ, increases as the temperature decreases and so can be measured with at least the same accuracy at the very lowest temperatures as at rather higher ones.

CHAPTER III

LIQUID AND SOLID HELIUM

THE determination of the physical properties of liquid and solid helium is an example of an investigation at lowest temperatures of particular interest, firstly because of the novelty of the phenomena observed and secondly because of the opportunity it affords of testing the predictions of the Nernst Heat Theorem.

Helium, the last of the so-called permanent gases to be liquefied, was first obtained in the liquid form by Kamerlingh Onnes in 1908. He found it to be a colourless, mobile, very volatile liquid which boils at 4·22° K. under a pressure of 1 atm. As already mentioned in Chapter I, Kamerlingh Onnes showed that helium remains a perfectly mobile liquid even when the pressure above the liquid surface is reduced to 0·013 mm. Hg and consequently the temperature is 0·82° K. This result indicated that there was very little prospect of obtaining solid helium by further lowering the vapour pressure of the liquid and that probably helium is noteworthy in not possessing a triple-point at which vapour, liquid and solid are in equilibrium. This conclusion was later confirmed when solid helium was obtained by Keesom.

An account will now be given of the results of the determinations of various physical properties of liquid helium, and the conclusions which can be drawn from them as to the nature of the substance will then be discussed.

DENSITY

The first indication, apart from the point just mentioned, that liquid helium possesses noteworthy and unusual physical properties, was obtained by Kamerlingh Onnes, who found that the density of the liquid passes through a maximum at about 2·2° K. More accurate determinations by Kamerlingh Onnes and Boks[1] later confirmed this observation. Their results are shown graphically in curve 1 of Fig. 10.* It will be seen that the density rises by about 20 per cent. as the temperature falls from 4·2° K. to 2·19° K., reaching a maximum of 0·1462 at 2·19° K. and at this temperature there is a sudden (probably discontinuous) change in the slope of the curve. The density then decreases as the temperature falls further and finally tends to become constant below 1·5° K.

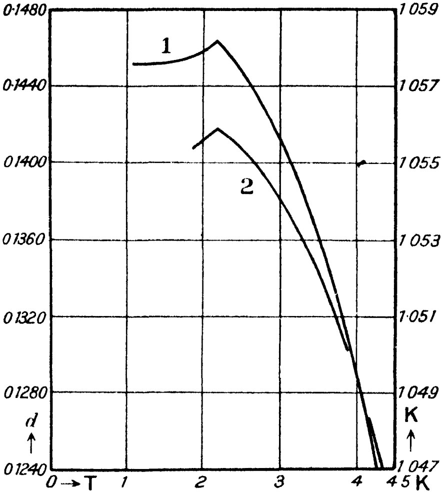

Fig. 10.

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* The value 2·3° K. given by Kamerlingh Onnes and Boks for the temperature at which the maximum occurs is based on an earlier determination of and an earlier formula for the vapour pressure-temperature curve of liquid helium. The form of the curve is that given by Wolfke and Keesom in the light of later results.

DIELECTRIC CONSTANT

The dielectric constant of liquid helium, according to the measurements of Wolfke and Keesom [2] given in curve 2 of Fig. 10, shows a strikingly similar behaviour. A calculation of the electrical polarization, using the formula, $P = \frac{K-1}{K+2} \cdot \frac{1}{d}$, shows, however, that this quantity does not change appreciably on passing through the temperature of the discontinuity, the values in the immediate neighbourhood of 2·19° K. being 2·24° K., P = 0·1242; 2·19°, 0·1245; 2·14°, 0·1242.

SURFACE TENSION

Van Urk, Keesom and Kamerlingh Onnes [3] determined the surface tension of liquid helium from 4·2° K. to 1·5° K. by the capillary tube method. Their results show that the surface tension rises linearly with fall in temperature down to 2·19°, possibly changes suddenly by a small amount at that temperature and finally tends to a constant value below about 1·5° K.

SPECIFIC HEAT

Preliminary determinations of the specific heat of liquid helium between 4·0° K. and 2·6° K. were made by Dana and Kamerlingh Onnes. Measurements of greater accuracy were made later by Keesom and Clusius [4] between 4·1° K. and 1·4° K., using the Nernst-Eucken method. In view of the very interesting results obtained the determinations were repeated and supplemented by Keesom and Miss Keesom.[5] The results obtained in the two series of experiments are shown graphically in Fig. 11.

C_s (the specific heat under the saturation vapour pressure at the temperature in question) increases with increasing temperature from 0·14 cals./deg. gm. at 1·32° K. to a very pronounced maximum of at least 3·0 at 2·19° K. It then falls suddenly, probably within 0·002°, to about 1·1, continues to fall more slowly to about 0·54 at 2·6° K. and finally rises again to 1·0 at 4·1° K. It was established that Fig. 11 does really represent the variation of C_s with temperature and that there is not a sudden evolution of heat at 2·19° K.

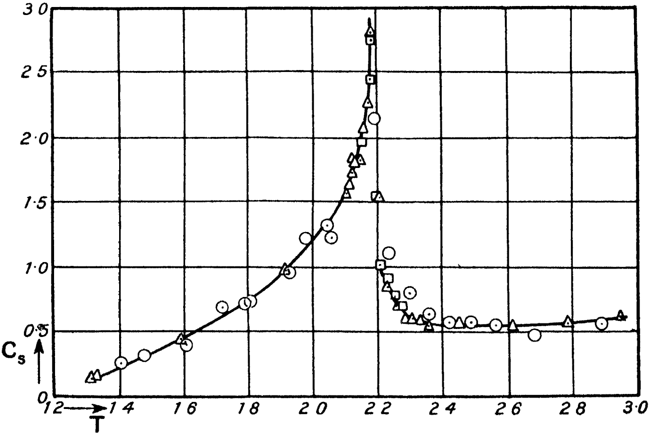

Fig. 11.

Latent Heat of Vaporization

Making use of the well-known thermodynamical formulæ,

$$\frac{dL}{dT} - \frac{L}{T} = C_s' - C_s''$$

$$\frac{dp}{dT} = \frac{L}{T(v' - v'')}$$

(L = latent heat of vaporization, p = vapour pressure, C_s', C_s'' specific heat at saturation of vapour and of liquid respectively, v', v'' specific volume of vapour and of liquid respectively), and combining them with the information available as to the quantities in the equation of state $pv = RT + B$, one can calculate the latent heat of vaporization of liquid helium from the data for C_s mentioned above. The values so calculated by Keesom are represented by the curve in Fig. 12. The experimental points shown are the data obtained by Dana and Kamerlingh Onnes.[6] The agreement is satisfactory ; in particular the anomaly found by these experimenters at about 2·19° K. is clearly indicated on the curve. Above 3° K. the experimental results show that the latent heat decreases with rise in temperature and falls to zero at the critical temperature, 5·2° K.

The extreme volatility of liquid helium and the consequent necessity for special precautions against heat entry if the liquid is to be preserved for any length of time are clearly brought out by the very small value of L, about 5·5 cal./gm. between 1·5° K. and 3·0° K. (Compare the values 110 cal./gm. for hydrogen at 20° K. and 536 cal./gm. for water at 373° K).

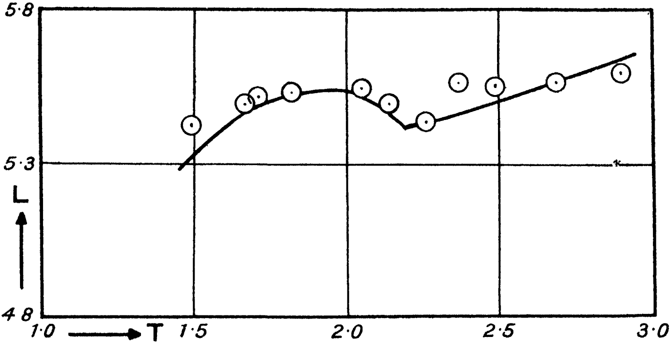

FIG. 12.

VAPOUR PRESSURE

In view of the great interest attached to the accurate determination and interpretation of the anomalous properties of liquid helium it is of considerable importance to establish the temperature scale in this region as accurately as possible. The variation with temperature of the properties of liquid helium just described make it improbable that a single formula can accurately represent the vapour pressure of this substance both above and below 2·19° K., the temperature at which the various anomalies occur. Keesom, Weber, Nørgaard and Schmidt [7] therefore redetermined the vapour pressure-temperature relation with great care from 4·22° K. down to 0·84° K. As mentioned in Chapter II they found that their results could best be represented by two separate formulæ, one for temperatures above 2·19° K. and one for temperatures below this, with a small discontinuity in the vapour pressure at 2·19° K. It was on the basis of these measurements that the temperature of the maximum density was fixed at 2·19° K. in place of the value 2·3° K. based on the older formula.

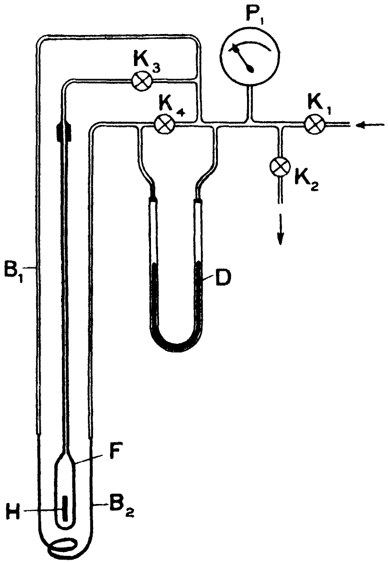

FIG. 13.

The significance of the results obtained in the determination of the various physical properties of liquid helium described above will be discussed later, after the description of the properties of solid helium.

SOLID HELIUM

As all the attempts to solidify helium by reducing the pressure under which liquid helium was boiling had failed, Keesom [8] in 1926 investigated the combined effect of high pressure and low temperature on the liquid. His apparatus is shown diagrammatically in Fig. 13. With the stop-cocks K_2 and K_4 shut and with stop-cock K_1 open, gaseous helium was compressed into the narrow nickel-silver tube B_1 and the brass capillary B_2. The

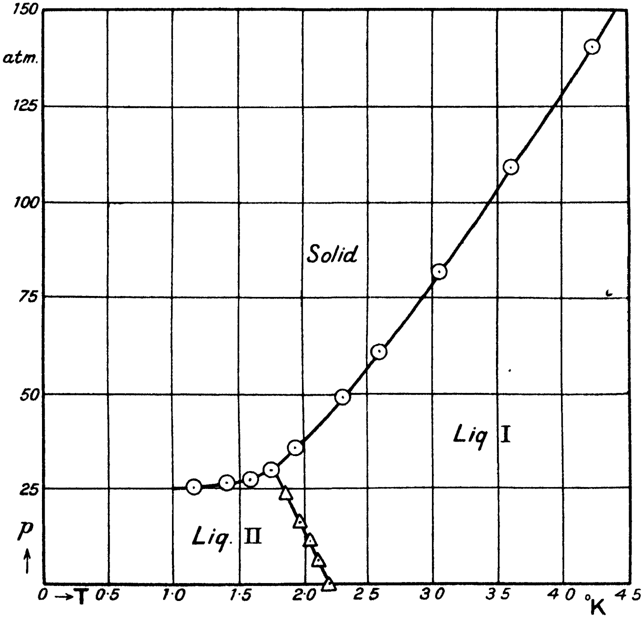

FIG. 14.

latter was immersed in liquid helium boiling at some known pressure. The helium liquefied and collected in B_2. To determine whether the helium solidified on further increasing the pressure, K_4 and K_1 were shut and K_2 opened. If now the helium had solidified the capillary B_2 would be blocked and on releasing the pressure by opening K_2 a difference of pressure would be registered by the differential manometer D. In this way it was found that at about 4·0° K. the capillary was blocked when the pressure, as read on the gauge P_1 was 150 kg./cm.^{2} and was open when the pressure was 100 kg./cm.^{2}. Raising the pressure to 128 kg./cm.^{2} caused the capillary to block again, on lowering the pressure to 126 kg./cm.^{2} the blocking disappeared. It thus appeared that at 4·0° K. helium solidifies under a pressure of 127 kg./cm.^{2}. Proceeding in this way it was possible to determine the pressure at which the helium solidified at various temperatures and so trace out the melting-curve of the substance. The results obtained are given in Table 4 and Fig. 14. It will be seen that while the curve is nearly linear at the higher temperatures, it bends more and more at lower temperatures and tends to become parallel to the temperature axis. Simon,[9] using the same general method, has extended the observations to 5600 atm. At this pressure helium "melts" at 42° K., a temperature very much higher than the liquid-gas critical temperature (5·2° K.).* Simon's observations also made it certain that helium solidifies to a definite crystalline substance and not to a super-cooled liquid or glass.

TABLE 4.

Melting Curve of Helium.

T.	P.
4·23° K.	140·5 atm.
3·60 „	108·8 „
3·09 „	81·5 „
2·63 „	62·8 „
2·30 „	48·6 „
1·93 „	35·7 „
1·74 „	29·8 „
1·58 „	27·4 „
1·40 „	26·5 „
1·15 „	25·3 „

After having shown that the pressures required to solidify helium below about 2° K. are not excessively high, Keesom repeated the observations with a thick-walled glass bulb F in order to render the solid helium visible. The bulb was provided with a stirrer in the shape of a small piece of soft iron H which could be moved up and down by means of a magnetized iron ring immersed in the liquid helium bath. Helium was liquefied into the bulb and the temperature set at 1·9° K. Then with the stirrer moving continuously up and down the pressure was gradually increased. At the pressure to be expected from the previous results, the stirrer was seen to stick. No line of demarcation between the liquid and solid was, however, visible. Helium thus solidifies to a homogeneous transparent mass, the refractive index and density of which are very nearly the same as those of the liquid at the same pressure.*

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* Above 5·2° K. the solid of course passes directly into the gaseous state when the pressure falls below the "melting" pressure.

THE NATURE OF LIQUID HELIUM I AND LIQUID HELIUM II

The results of the determinations of the density and dielectric constant of liquid helium lead Keesom and Wolfke to suggest that at 2·19° K. this substance changes from one phase to another also liquid phase, stable below this temperature. The two phases were referred to as liquid He I and liquid He II and the transition temperature as the λ-point.

By taking cooling-curves with liquid helium subjected to various external pressures in the calorimeter used to determine the specific heat, Keesom and Clusius[10] found that the λ-point varies with the pressure as given in Table 5. These points are plotted in curve 2, Fig. 14 (the λ-curve), and it will be seen that they lie on a straight line which, when extrapolated, cuts the melting-curve at 30·0 atm. and 1·75° K. This point is thus a triple-point in the P.T. diagram, and the curves meeting in it separate regions in which

TABLE 5

P (atm.).	T.
0·051	2·19
6·39	2·11
11·13	2·05
16·09	1·97
23·60	1·86

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* Kaischew and Simon have recently measured the density of solid helium and give $d = 0{\cdot}23$ at 4·0° K. and 0·22 at 3·6° K.

solid He, liquid He I and liquid He II exist. Keesom and Miss Keesom[11] have further shown that the phenomenon of the maximum density of liquid helium persists all along the λ-curve, becoming more and more pronounced as the " triple "-point is approached. Their observations also indicate that the coefficient of expansion and the compressibility of liquid He II are both negative throughout the range of existence of this phase. This remarkable result has a very direct bearing on the proposal for obtaining very low temperatures with liquid helium by the " method of external work " as mentioned in Chapter I. Isentropic and isenthalphic expansions of liquid He II both result in a rise in temperature.

We can now discuss the nature of liquid He II in the light of its physical properties ascertained up to now. The fact that the curves of density and latent heat of vaporization show no discontinuity at the λ-point (only the slope of the curve changes discontinuously) indicates that there is no change of volume or of entropy in the transition from liquid He I to liquid He II. This indicates that the two forms of liquid helium are not two " phases " in the sense in which this word is used in that branch of thermodynamics which is known as the Phase Theory and which studies the effect of various physical conditions (temperature, pressure, etc.) on the equilibrium between the possible forms of the substances present in a physico-chemical system. In the transformation of one such phase into another (for example ice $\overset{0^\circ\text{ C.}}{\rightleftharpoons}$ water or $Na_2SO_4 \overset{32{\cdot}4^\circ\text{ C.}}{\rightleftharpoons} Na_2SO_4 \,.\, 10H_2O$) there is always a change in volume and a heat of transformation (change in entropy). Ehrenfest[12] therefore proposes to call the kind of transformation exhibited by liquid helium a " phase transformation of the second order " and he shows that the transition from the ferromagnetic to the paramagnetic state at the Curie Point and from ordinary conductivity to superconductivity (see Chapter V) are further examples of such transitions.

Exactly what happens in the transformation of liquid He I into liquid He II is as yet quite obscure. Liquid He I appears to be a normal liquid, which is at least predominantly, if not exclusively, monatomic. That the change at the λ-point is not merely one of association of atoms to form molecules is shown by the fact that liquid He II gives no Raman effect. McLennan's[13] observations indicate that the temporary formation of loosely bound molecules with a very large internuclear distance may occur but nothing more definite. Further, the electric polarization deduced from the measurements of the dielectric constant does not change appreciably on passing the λ-point. There is therefore no important change in the atomic structure.

The shape of the melting-curve of solid helium below 1·75° K. furnishes very important and definite information bearing on the nature of liquid He II. The slope $dp/d\mathrm{T}$ of the curve is rapidly approaching zero in this region and at, for example, 0·71° K., the lowest temperature so far reached with liquid helium, the slope is very small. Since now, according to the Clausius-Clapeyron equation

$$\frac{dp}{d\mathrm{T}} = \frac{\mathrm{L}}{\mathrm{T}(v_1 - v_2)} = \frac{\phi_1 - \phi_2}{v_1 - v_2}$$

(ϕ_1, ϕ_2 entropies, v_1, v_2 spec. vols. of liquid and solid respectively), and since $v_1 - v_2$ is small though finite, the difference in entropy of solid He and liquid He II at this temperature must be very small indeed. Entropy is, however, statistically interpreted as giving the orderedness of a substance. The above result therefore means that liquid He II has practically the same degree of orderedness at 0·71° K. as solid helium although the former is a mobile liquid and the latter a definitely crystalline solid. This problem of the quasi-crystalline nature of liquid He II is as yet unsolved.

The specific heat curve (Fig. 11) furnishes further information but without any accepted explanation. By extrapolating the two branches of the curve to absolute zero and determining the area enclosed between them, one can calculate the difference in the energy which liquid He II possesses and that which liquid He I would possess if it could exist at the Absolute Zero. Assuming a molecular weight of 4 for liquid He II, this energy difference is found to be about 2·3 cal./gm. mol. This low value is in agreement with other results in showing that no large change in atomic structure has taken place.

The mechanism underlying the anomaly in the specific heat is not yet understood, but a precisely similar anomaly has been observed in two other cases, the specific heat of a ferromagnetic substance in the neighbourhood of the Curie Point and the specific heat of certain solids containing polyatomic molecules (ammonium chloride, methane, etc.). It may therefore be that the atoms in liquid He II are able to take up energy in some form as yet unknown and which varies with the temperature in the same way as the spontaneous magnetization of a ferromagnetic substance. On the other hand, it is just possible that, as liquid He II is quasi-crystalline and as there may be at least some loosely bound molecules present, the anomaly is of the same kind as that of the polyatomic solids. Pauling has shown that such an anomaly is to be expected theoretically if the molecules or parts of them pass suddenly at a certain temperature from a state of angular oscillation to one of rotation in the crystal lattice. Experimental evidence of the reality of these molecular rotations in the solids showing the anomalous specific heat curves has since been obtained.

HELIUM AND THE NERNST HEAT THEOREM

According to the Nernst Heat Theorem dF/dT, where F is the change of the free energy,* approaches zero as T approaches zero for changes taking place in condensed systems, i.e. liquids and crystalline solids. This theorem implies that the derivatives with respect to the temperature of certain physical quantities must also approach zero as T approaches zero and that any changes taking place between condensed systems at Absolute Zero do so without change in entropy.

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* See Porter, "Thermodynamics," p. 41.

The physical properties of liquid and solid helium so far determined furnish very direct evidence of the correctness of the Nernst Heat Theorem. Thus the density and the surface tension of liquid helium both tend to become independent of the temperature below about 1·5° K. so that $\frac{dv}{d\mathrm{T}} \rightarrow 0$ and $\frac{d\psi}{d\mathrm{T}} \rightarrow 0$ as $\mathrm{T} \rightarrow 0$ in accordance with the theorem.

Further, we have seen that the melting-curve of solid helium also tends to become parallel to the temperature axis as $\mathrm{T} \rightarrow 0$, i.e. $\frac{dp}{d\mathrm{T}} \rightarrow 0$ as $\mathrm{T} \rightarrow 0$. Since now $\frac{dp}{d\mathrm{T}} = \frac{\Delta\phi}{\Delta v}$ ($\Delta\phi$ = change in entropy, Δv = change in volume on melting), and since Δv is finite at $\mathrm{T} = 0$, we have in agreement with the Nernst Heat Theorem $\Delta\phi \rightarrow 0$ as $\mathrm{T} \rightarrow 0$. The transformation of solid helium into liquid helium will take place at the Absolute Zero without change in entropy.

CHAPTER IV

SPECIFIC HEATS

The specific heats of gases and solids will now be discussed as an example of calorimetry at low temperatures.

Gases

Two general methods have been employed for the determination of the specific heats of gases down to very low temperatures, the continuous flow method and the Nernst-Eucken method, using compressed gas.

In determining the specific heat of gases by the continuous flow method, Scheel and Heuse[1] made use of the apparatus shown in Fig. 15. Gas at the temperature at which the specific heat is to be determined enters the glass calorimeter at the bottom, flows through the spiral, then through the two jackets C and B and finally through the tube A containing the heating coil. The temperature of the gas before and after the heating are determined with the platinum thermometers P_1 and P_2 respectively. The whole is surrounded by a silvered evacuated jacket to reduce heat loss and is contained in a bath of constant temperature (water, solid CO_2 and alcohol or liquid oxygen). The jackets B and C

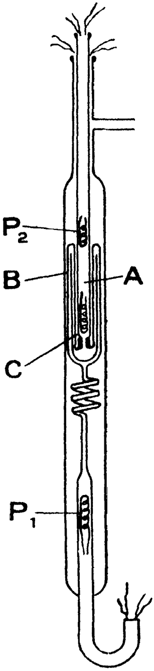

Fig. 15.

also serve to reduce the heat loss from the gas. The experiments were carried out at room temperature, −76° C. and −181°.

If the quantity of gas flowing through the calorimeter per second is Q, the heat input per second H and the rise in temperature Δt, then

$$C_p = \frac{H - h}{Q \, . \, \Delta t} . \qquad (1)$$

h = heat input required to balance loss through walls. Some of the results obtained are given in Table 6. C_{p_0} is the specific heat at constant pressure corrected for the deviations from the perfect gas law. C_{v_0} was obtained from the (corrected) observed C_p, using well-known thermodynamical formulæ. It will be seen that while the specific heat of the monatomic gas helium remains fairly constant, that of the diatomic gases falls considerably with decrease in temperature.

TABLE 6

Substance.	T.	C_{p_0}.	C_{v_0}.
He	+ 18	4·993	3·008
	−180	4·934	2·949
H_2	+ 16	6·860	4·875
	− 76	6·364	4·379
	−181	5·320	3·335
N_2	+ 20	6·969	4·984
	−181	6·718	4·733

The application of the vacuum calorimeter to the determination of the specific heats of gases at low temperatures may be illustrated by the work of Eucken and Hiller [2] on hydrogen. The small steel bulb A (Fig. 16) is filled with gas at 150 atmospheres through the fine capillary K. On the outside of A is wound a constantan heating coil and a platinum resistance thermometer.

The metal cylinder B surrounding A serves to minimize heat loss and is maintained at the same temperature as A by a current in a heating coil wound on B, the equality of the temperatures being indicated by a copper δ-constantan thermocouple whose junctions are attached to A and B respectively. The whole is enclosed in a glass vessel D which can be evacuated. D is evacuated and the current in the heating coil switched on for a known length of time.

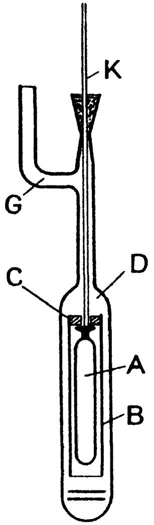

FIG. 16.

The general trend of the variation of the specific heats of diatomic molecules will be illustrated by the case of hydrogen which is of particular interest. The earlier results of Eucken (1912) are given in Table 7 and are plotted along with those of Eucken and Hiller and others (for C_R, see later) in Fig. 17. It will be seen from Table 7 that the specific heat of hydrogen falls off rapidly with decrease in temperature and becomes nearly constant and equal to 2·98 below 60° K.

TABLE 7

T.	C_{v_0}.
196·5° K.	4·39
100	3·42
80	3·14
60	2·99
45	3·00
35	2·98

The classical theory indicates that a gas possesses an energy $\frac{1}{2}$RT per degree of freedom per gm. mol. The contribution to the specific heat C_v of the translational energy is therefore 3/2 R = 2·98 and the specific heat at constant volume of monatomic gases should have this value. The results of Scheel and Heuse show that this is approximately the case with He and Ar. Below 60° K. hydrogen thus behaves as a monatomic gas in that only the translational energy contributes to C_v. In general, however, a diatomic molecule will also possess rotational energy and classically the contribution of the rotation to the specific heat, C_R, will be $2/2$ R and therefore independent of the temperature. According to the quantum theory the rotational energy of a diatomic molecule is $E_R = n^2 . \frac{h^2}{8\pi^2 I}$, in which I is the moment of inertia and the quantum number n may have the values 0, 1, 2, 3, etc. At very low temperatures only the lowest rotational state ($n = 0$ or 1 according to the type of molecule) will be occupied and the higher states will only

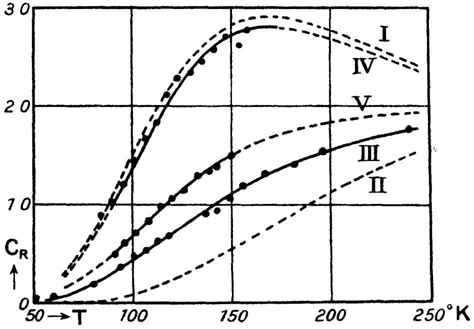

FIG. 17.

begin to be occupied as the temperature rises. C_R will therefore vary with temperature. It can be shown that C_R for a diatomic molecule is given by

$$C_R = \sigma^2 . R . \frac{d^2}{d\sigma^2} (\log Q), \quad . \quad . \quad (2)$$

in which $\sigma = \frac{h^2}{8\pi^2 I k T}$ and Q is a function of σ.

By subtracting 2·98 from the observed values of C_v one can obtain C_R from Eucken's results.* When the experimental values were compared with expression (2) no satisfactory agreement could be obtained with any value of I. Later, however, the wave mechanics indicated that hydrogen can exist in two forms, ortho- and para-hydrogen, which differ in the magnetic moments of the nuclei of the two hydrogen atoms, being parallel in ortho-hydrogen and antiparallel in para-hydrogen. Furthermore, theory showed that at room temperature ordinary hydrogen consists of a mixture of ortho- and para-hydrogen in the ratio 3 : 1 and that the transformation of the one form into the other is very slow at these temperatures. Dennison was then able to show that Eucken's results for C_R could be explained satisfactorily by supposing that no transformation of ortho- into para-hydrogen took place during the time required to make the observations and that therefore the two forms could be taken as independent. The specific heat of ordinary hydrogen then becomes

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* Eucken's observations show that C_v falls below 2·98 at about 20° K. This result, which is known as the degeneration

$$C_R = \frac{\rho C_{R(p)} + C_{R(o)}}{1 + \rho}, \quad . \quad . \quad (3)$$

in which $\rho = \frac{1}{3}$ and

$$C_{R(p)} = \sigma^2 \,.\, R \,.\, \frac{d^2}{d\sigma^2}(\log Q_{(p)}), \quad . \quad . \quad (4)$$

with $Q_{(p)} = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \ldots$

corresponding to $n = 0, 2, 4$, etc., and

$$C_{R(o)} = \sigma^2 \,.\, R \,.\, \frac{d^2}{d\sigma^2}(\log Q_{(o)}), \quad . \quad . \quad (5)$$

with $Q_{(o)} = 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \ldots$

corresponding to $n = 1, 3, 5$, etc.

Curves I, II and III of Fig. 17 represent expressions (4), (5) and (3) respectively, taking I to be $4{\cdot}64 \times 10^{-41}$, a value in good agreement with that deduced by Hori from spectra ($4{\cdot}67 \times 10^{-41}$). It will be seen that the

of gases, can be explained by applying the quantum theory to the translational energy of the molecules. Helium shows a similar result.

experimental values for C_R in the case of ordinary hydrogen agree well with curve III.

It has also been found possible by keeping hydrogen for a considerable time at a low temperature with or without a catalyst to increase the para-hydrogen content and even to obtain pure para-hydrogen. Curves IV and V represent the theoretical course of C_R for mixtures of higher para-hydrogen content, the experimental points being Eucken and Hiller's observations on these mixtures. It will be seen that the theory can reproduce the experimental results in a very satisfactory way.

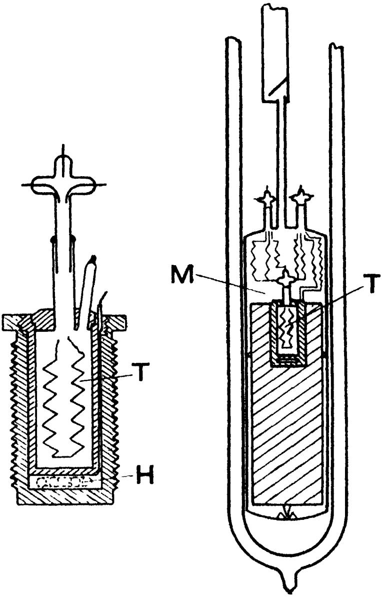

Fig. 18.

The rotational specific heat of other diatomic gases which consist of only one molecular species can be theoretically accounted for by formula (2) with the appropriate value of I.

At low temperatures the vibrations of the atoms in the molecule are not excited and hence the contribution of the vibrational energy to the specific heat of gases will not be considered here.

Solids

The specific heats of solids at very low temperatures have been determined almost exclusively by means of the vacuum calorimeter developed by Nernst, Eucken and their collaborators. The calorimeter is differently constructed according to the nature of the substance to be investigated. Fig. 18 shows its most recent form for the determination of the specific heat of metals at helium temperatures (Keesom).[3] A block of the metal has a tapped recess into which is screwed the " core " shown in detail on the left. The core contains a phosphor-bronze and a constantan resistance thermometer T and a constantan heating coil H. The leads to the heating coil and thermometers are taken through the small glass crosses as shown. The whole calorimeter is enclosed in a metal vessel M which can be evacuated and which is immersed in liquid helium in the Dewar vessel shown. For determining the specific heats of powdered solids or solidified gases the calorimeter is made of thin sheet silver or copper (Fig. 19), the heating coil and thermometer being inserted into the vessel as shown in I or wound on the outside, II. When dealing with powders the vessel is sealed off with a small pressure of helium inside to increase the heat conductivity and promote uniformity of temperature throughout the powder.

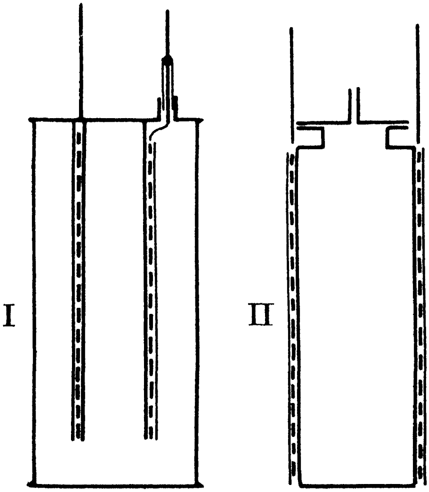

Fig. 19.

In order to determine the specific heat the calorimeter is allowed to cool to the lowest temperature required, the space surrounding the calorimeter is then evacuated and a known current is passed through the heating coil for a known length of time. The temperature of the calorimeter is measured at definite intervals before, during and after the heating period and a temperature-time curve such as Fig. 20 is obtained. The true rise in temperature to be used in calculating the specific heat can be obtained in various ways, the simplest but not the most accurate being to draw the ordinate through C so that the areas ADC and BEC are equal. AB is then the true rise in temperature. The heating current may then be switched on again and an observation made at a higher temperature until the required range has been covered.

The experimental results show that the specific heats of solids, apart from special cases discussed later, vary with the temperature in the general way shown in Fig. 21, falling from a value of approximately 6 cal. per deg. per gm. atom (for the elements) at high temperatures to very small values at helium temperatures (0·000254 cal. per gm. atom for Ag at 1·35° K. for example), to become zero at the Absolute Zero.

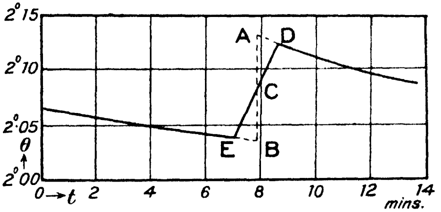

FIG. 20.

According to the classical mechanics the atomic heat (specific heat × atomic weight) of a monatomic solid element should be independent of the temperature and equal to 3R or approximately 6 cal. per deg. The explanation of the observed fall in the specific heat of solids at low temperatures was one of the early successes of the quantum theory. By assuming that all the atoms in the solid are vibrating with a frequency ν (due to their of freedom of the atom an energy $E = h\nu/e^{h\nu/kT} - 1$ as required by the quantum theory in place of $kT(\frac{1}{2}kT$ potential energy $+\ \frac{1}{2}kT$ kinetic energy), Einstein obtained the following formula for $C_v \left(= \left(\frac{\partial E}{\partial T}\right)_v \right)$:—

$$C_v = 3R \, . \, \frac{e^{\theta/T}\left(\frac{\theta}{T}\right)^2}{(e^{\theta/T} - 1)^2}, \qquad \qquad (6)$$

$\theta = h\nu/k$, $R = Nk$, $N =$ number of atoms in gm. atom. This expression gives a good qualitative representation of the variation of the specific heat of solids * with the temperature. By discarding the too simple assumption that all the atoms vibrate with the same frequency ν, Debye was able to deduce a formula which gives a generally very satisfactory representation of the experimental results down to low temperatures :—

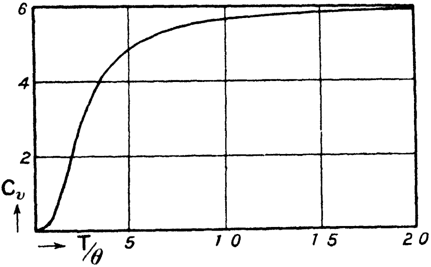

FIG. 21.

$$C_v = 3R\left\{12\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{e^x - 1}dx - \frac{3\left(\frac{T}{\theta_D}\right)}{e^{\theta_D/T} - 1}\right\} \qquad (7)$$

in which $x = \frac{h\nu}{kT}$, $\theta_D = \frac{h\nu_m}{k}$.

---

* The experimentally determined quantity is C_p. C_v can be obtained from C_p by means of various theoretical or empirical formulæ, such as $C_p - C_v = T\alpha^2V^2/\chi C_v$, in which $\alpha =$ coefficient of cubic expansion, $\chi =$ compressibility, $V =$ atomic volume.

All atomic frequencies from 0 up to a maximum value ν_m are now taken to be possible and the energy of the solid becomes $E = \int_0^{\nu_m} [h\nu/(e^{h\nu/kT} - 1)] n(\nu) d\nu$, in which $n(\nu)$ is the number of frequencies lying within the range ν and $\nu + d\nu$. Debye considers the substance as a homogeneous elastic solid and assumes that the heat motions of the atoms can be represented by the sum of all the possible elastic waves which can occur in the solid. From the theory of elasticity the number of independent vibrations (elastic waves) whose frequencies lie between ν and $\nu + d\nu$ can be calculated. In order to determine the maximum frequency, ν_m, Debye equates the total number of independent vibrations possessed by a gm. atom of the solid to 3N, the total number of degrees of freedom. (For an infinitely extended solid the number of independent vibrations would be infinite.) Then $\int_0^{\nu_m} n(\nu) d\nu = 3N$. In this way, using the value of $n(\nu)$ given by elastic theory, the magnitude of $\theta_D = h\nu_m/k$ can be calculated. Debye thus obtains the expression

$$\theta_D = \frac{3{\cdot}6 \times 10^{-3}}{A^{\frac{1}{3}} \rho^{\frac{1}{6}} \chi^{\frac{1}{2}} [f(\sigma)]^{\frac{1}{3}}},$$

where A = atomic weight, ρ = density, χ = compressibility, $f(\sigma)$ = a function of σ, Poisson's ratio.

It is found that the Debye formula (7) fits well the observed specific heats of the elements except at extremely low temperatures. Table 8 gives a comparison between the experimental and theoretical values for aluminium.

TABLE 8

Aluminium, $\theta_D = 398$

T.	C_p (obs.).	C_p (calc.).
32·4	0·25	0·25
35·1	0·33	0·32
83·0	2·41	2·36
86·0	2·52	2·50
88·3	2·62	2·59
137·0	3·97	4·10
235·0	5·32	5·34
331·0	5·82	5·78
433·0	6·10	6·07
555·0	6·48	6·30

Table 9 gives the values of θ_D obtained for a number of elements, columns 2 and 3 the experimental value deduced from the observed specific heat at ordinary and high, and very low temperatures respectively, column 4 the calculated values using Debye's expression, columns 5 and 6 theoretical values calculated from formulæ given by Grüneisen (from cœfficient of cubic expansion) and Lindemann (from melting-point) respectively.

TABLE 9

Element.	θ_D (exp.).		θ_D (calc.).		
	Higher Temps.	Very Low Temps.	Debye.	Grüneisen.	Lindemann.
Ag	217	210	212	210	196
Cu	315	320	329	325	302
Cd	160	129	168	148	123
Al	398	385	399	374	342
Pb	88	84	72	103	82
C (diamond)	1840	2230	—	1860	1450

In comparing the observed values with the calculated ones for the specific heat of compounds it is necessary, except at very low temperatures, to combine a Debye curve (to represent the contribution to the specific heat of the translational motion of the molecules as a whole) and an Einstein curve (to represent the contribution of the internal vibrations of the molecule, which in the case of a diatomic molecule such as NaCl at any rate, can be supposed to occur with a definite frequency ν deducible from the properties of the molecule).

According to expression (7) the specific heats of all solids, which satisfy the assumptions of the theory, should lie on the same curve if plotted against T/θ_D instead of T; that is the specific heat is a universal function of T/θ_D. Fig. 21 shows the Debye curve plotted as a function of T/θ_D. Schrödinger[4] has shown that the observed specific heats of a large number of solids do indeed accurately lie on this curve.*

At sufficiently low temperatures Debye's formula reduces to

$$C_v = 464{\cdot}5\left(\frac{T}{\theta_D}\right)^3 = \text{const.} \times T^3. \qquad . \quad (8)$$

This simplified expression fits well the experimental values for a large number of substances, and is of importance as it has been extensively used to extrapolate to the Absolute Zero in cases where the heat content of bodies, $\int_0^T CdT$, is required. Since the internal vibrations of the molecules of any substance are not excited below a certain temperature dependent on the nature of the substance, the Debye T^3 law holds whether the substance is an element or a compound, provided this characteristic temperature is not exceeded.

The specific heats of lead, bismuth, tin, zinc, thallium and silver have recently been measured by Keesom[3] down to very low temperatures, mostly with the aid of the apparatus shown in Fig. 18. In order to test the applicability of Debye's formula and to show up any possible deviations from it, the value of θ_D was calculated from the formula for each experimental point. It was then seen that while lead obeys the T^3 law almost accurately down to 3° K., relatively large deviations occur in the case of the other metals. θ_D shows a tendency to rise to a maximum below 5° K. and fall considerably at lower temperatures. The origin of these deviations is not yet definitely known, but it is likely to lie in the contribution of the conduction electrons to the specific heat. This contribution, according to the Sommerfeld and Bloch theories of conduction, is small at room temperature, but as it varies at low temperatures as the first power of the temperature it becomes comparable with the observed specific heats at temperatures below about 5° K. It would be of considerable interest to determine the specific heats of various non-metallic elements at helium temperatures and so throw light on this point. The fact that solid para-hydrogen follows the Debye law, with θ_D equal to 91 down to 2° K. (see p. 61), furnishes support for the explanation mentioned above for the deviations observed with the metallic elements.

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* The curve, together with the experimental points, is reproduced in Roberts' "Heat and Thermodynamics," data being given for Al, Ag, C, Ca, Cd, Cu, Fe, Hg, I, Na, Pb, Tl, Zn, CaF_2, FeS_2, NaCl, KBr, KCl. The very numerous experimental points are omitted from Fig. 21 as they could not be adequately shown on a small diagram.

The specific heats of tin and thallium are noteworthy in that they show a sudden jump on passing through the temperature at which these elements become superconducting (see Chapter V). A similar jump has not been observed with lead (Simon, Keesom), although it also becomes a superconductor at 7·26° K. If however the actual jump were of the same absolute magnitude as it is in tin (0·0024) it would only be about 1 per cent. of the observed atomic heat of lead at 7° K. and so would be of the same order of magnitude as the experimental error.

The quantum theories of specific heat are based on the assumption that all the atoms or molecules remain throughout in their "ground state" (the electronic state of the atom or molecule which possesses the lowest energy). If there is also another possible atomic or molecular state with an energy ΔE above the ground state, then at Absolute Zero all the atoms or molecules will be in the lowest state, but as the temperature rises the upper state will also begin to be occupied. The number of atoms in the upper state at any temperature T is given by statistical theory as $n = n_0 e^{-\Delta E/kT}$, where n_0 is the number of atoms in the ground state, so that at an infinitely high temperature there will be an equal number of atoms in both states. Some of the heat put into the body will therefore go into raising some of the atoms from the ground state to the upper state instead of increasing the translational energy of the atoms, and the apparent specific heat will consequently be greater than in the absence of this effect. Schottky[5] has shown that the additional term to the specific heat, ΔC, which results from increasing the population of the upper state is given by

$$\Delta C = \frac{k\left(\frac{\Delta E}{kT}\right)^2 e^{\Delta E/kT}}{(1 + e^{\Delta E/kT})^2}. \qquad (9)$$

This expression gives a bell-shaped curve which rises from zero at the Absolute Zero to a maximum at a temperature dependent on the magnitude of ΔE and then decreases to zero at higher temperatures. The observed specific heat will then be the sum of C_v and ΔC.

The specific heats of gaseous nitric oxide, gadolinium sulphate and solid ortho-hydrogen show anomalies which can be represented by Schottky's formula (9). Thus it is known from a study of the spectrum emitted by nitric oxide that the normal state of the NO molecule is a $^2\Pi$ state, the components ($^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$) being separated by an energy difference of 354 cals. At very low temperatures all the molecules will be in the lower ($^2\Pi_{\frac{1}{2}}$) state but at room temperature the numbers of molecules in the two states will be nearly equal. Eucken and d'Or[6] have measured C_p for nitric oxide over the range of temperature 127°-288° K. and find that the specific heat decreases nearly linearly with rise in temperature, thus the opposite behaviour to the normal in this range. The experimental values, however, agree well with the sum of the normal specific heat of a diatomic gas having the known moment of inertia of the nitric oxide molecule and ΔC of expression (9), provided ΔE is taken to be 354 cals. as required by spectroscopic data.

The specific heat of crystalline gadolinium sulphate has been measured by Kurti[7] from 1·6° to 20° K. (and also by Giauque and MacDougall[8] down to 0·27° K.). Down to 7° K. the Debye T^3 is obeyed, but below this temperature the specific heat curve begins to turn upwards until at 1·6° K. the specific heat is 500 times as great as the value given by extrapolating the T^3 curve to this temperature. The additional specific heat, given by subtracting the values of the T^3 law from the observed ones, can be explained as a Schottky effect. The ground state of the gadolinium ion Gd^{+++} is an $^8S_{\frac{7}{2}}$ state, which therefore consists in the absence of any external magnetic or electric field of eight superposed levels of the same energy. In the presence, however, of the non-uniform electrostatic field of the surrounding ions this will no longer be the case and the eight levels will possess different energies, being separated from each other by an approximately equal energy difference, ΔE. Attributing the whole of the anomaly to the Schottky contribution of the gadolinium ion, Kurti's observations can be explained if $\Delta E = 0{\cdot}52$ cal. This would indicate that the maximum of the Schottky curve would occur at about 0·1° K. The small value for ΔE is entirely in accord with expectation, as the separation of the eight sub-levels of the $^8S_{\frac{7}{2}}$ ground state by the electrostatic field of the crystal is only a second order effect.

The measurements of Simon, Mendelssohn and Ruhemann [9] on solid hydrogen between 2° and 20° K. show that while solid para-hydrogen obeys well the Debye law with $\theta_D = 91$, that of solid ortho-hydrogen (deduced from measurements on mixtures of known proportions of ortho- and para-hydrogen) deviates markedly therefrom below 12° K. The course of the deviation agrees with what would be expected from the Schottky effect if it is assumed that the ortho molecules in the solid possess three neighbouring energy states, distant 7·5 cals. from each other.

Another type of deviation from the Debye curve which deserves mention is that shown by solid methane, solid hydrogen bromide and various ammonium salts. Clusius [10] has shown that the specific heat of solid methane begins to rise very rapidly in the neighbourhood of 20° K., reaches a maximum of more than 80 cals. per deg. per gm. mol. at 20·44° K. and then falls rapidly to about 4·6 cals. per deg. per gm. mol. at 21·2°. The specific heat-temperature curve then becomes normal up to the melting-point. The anomaly is therefore similar to that shown by liquid helium (Fig. 11), but with a much more pronounced maximum. Pauling has suggested that this anomalous behaviour is due to the molecules (or parts of the molecule) of the solid substance passing fairly suddenly from oscillation to free rotation in the crystal. It is, however, difficult to see that such an effect, if this is the whole explanation, will give such a rapid change in the specific heat as is observed unless a coupling between the rotating molecules is assumed, one molecule beginning to rotate causing its neighbours to rotate also. Quantitative calculations of the effect have not yet been made.

CHAPTER V

ELECTRICAL CONDUCTIVITY

THE variation with temperature of the electrical conductivity of the metallic elements and of alloys has been the subject of very many investigations. The results show that electrical conductors fall naturally into three groups: (1) the pure metals, intermetallic compounds and certain alloys, for which the specific resistance varies approximately as the absolute temperature at about room temperature; (2) certain other alloys such as eureka and manganin, for which the specific resistance is nearly independent of the temperature at about room temperature; and (3) semi-conductors such as carbon and cuprous oxide, for which the specific resistance generally increases as the temperature decreases.

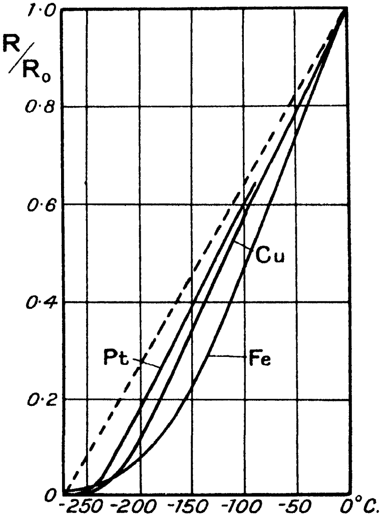

FIG. 22.

The general form of the specific resistance-temperature curve for the pure metals, which crystallize in the cubic system, is typified by the examples given in Fig. 22, in which the abscissæ represent $r = \rho/\rho_0$, the specific resistance at the temperature T divided by that at 0° C. At not too low temperatures the resistance decreases approximately linearly but more rapidly than is given by $\rho \propto T$. At very low temperatures the specific resistance of all " pure " metals tends to become independent of the temperature, as shown in Figs. 22 and 23. The various curves in the latter figure show the variation of the specific resistance of specimens

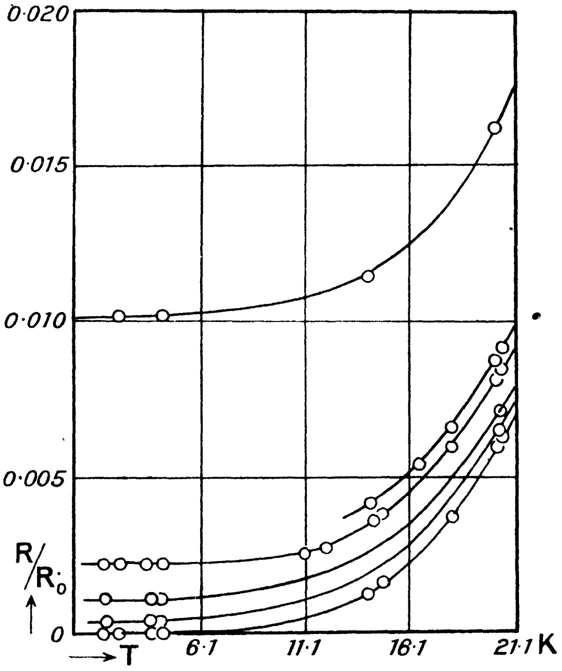

Fig. 23.

of gold of different degrees of purity. All the specimens have a certain "residual resistance" (the resistance obtained by extrapolating the curves to Absolute Zero), this residual resistance being greater the greater the amount of impurity present in the specimen and being also greater if the metal is strained or deformed in any way. The course of the resistance-temperature curve for an ideal strain-free metal can be deduced with the aid of the Mathiessen-Nernst rule, $r = \frac{r_{\text{obs.}} - c}{1 - c}$, where $r = \rho/\rho_0$ for the ideal metal and c is a constant. The lowest curve of Fig. 23 shows the agreement among the values of r obtained by means of the above formula from the observations on the various specimens. All experimental values of the specific resistance of the "pure" metals must be reduced in this way before being compared with theory. On account of the enormous influence of minute amounts of impurity on the resistance of the metallic elements at very low temperatures relatively few of the published data are of any value for comparison with theoretical formulæ. For this reason we will quote only a few illustrative examples taken mainly from Meissner's[1] observations on very pure specimens (Meissner's single crystal of gold, Au 11, contained for example less than 0·001 per cent. of impurity). In the following tables the ob-

TABLE 10

Copper, $\theta = 330$

T.	$r_{\text{calc.}}$	$\frac{r_{\text{obs.}} - 0{\cdot}0003}{1 - 0{\cdot}0003}$.
273·2	1	1
195·2	0·662	0·658
90·2	0·1847	0·1804
81·2	0·1451	0·141
20·4	0·00059	0·00051
4·2	0·00000	0·00000

TABLE 11

Lead, $\theta = 88$

T.	$r_{\text{calc.}}$	$\frac{r_{\text{obs.}} - 1{\cdot}55 \times 10^{-4}}{1 - 1{\cdot}55 \times 10^{-4}}$.
273·16	1	1
20·32	0·03058	0·02905
14·02	0·01003	0·01025
7·26	0·00057	0·00060
4·2	4×10^{-8}	2×10^{-8}

TABLE 12

Gold, $\theta = 175$

T.	$r_{\text{calc.}}$	$\frac{r_{\text{obs.}} - 0{\cdot}00029}{1 - 0{\cdot}00029}$. (Meissner.)	$\frac{r_{\text{obs.}} - 0{\cdot}00223}{1 - 0{\cdot}00223}$ (Onnes and Clay.)
273·2	1	1	1
87·43	0·2645	0·2551	—
78·86	0·2276	0·2187	—
57·8	0·1356	—	0·1314
20·4	0·00604	0·00572	0·0059
18·0	0·00346	—	0·0035
14·3	0·00117	—	0·00137
12·1	0·00051	—	0·00048
11·1	0·00033	—	0·00030
4·2	$0{\cdot}000002_6$	$0{\cdot}00000_3$	—

TABLE 13

Tungsten, $\theta = 346$

T.	$r_{\text{calc.}}$	$\frac{r_{\text{obs.}} - 0{\cdot}00058}{1 - 0{\cdot}00058}$.
273·2	1	1
90·2	0·176	0·168
87·4	0·163	0·156
77·6	0·122	0·115
20·4	0·00049	$0{\cdot}0005_0$

served values of ρ/ρ_0, reduced according to the Mathiessen-Nernst rule, are compared with a semi-empirical formula of Grüneisen for the metals copper, gold, lead and tungsten. The significance of $r_{\text{calc.}}$ will be given later in the discussion of the theories of electrical conductivity at low temperatures.

The resistance of lead below 7·26° K. (the temperature at which this substance becomes superconducting, see p. 73) was obtained from the resistance observed in the presence of a magnetic field. The recorded data were obtained by extrapolating the observed resistances to $H = 0$. Meissner's data on lead are included because this specimen shows the smallest recorded value of the residual resistance and so should be most directly comparable with the ideal metal considered in the theoretical treatment of electrical conduction.

The variation with temperature of the specific resistance of dilute alloys, the constituents of which are completely miscible in one another, may be illustrated from the data given by Clay [2] for gold-silver alloys (Table 14).

TABLE 14

Specific Resistance of Au—Ag *Alloys*

Vol. Per Cent. Ag.	Temp. °C.	$\rho_{\text{obs.}} \times 10^9$.	$\rho_m \times 10^9$.	$\xi \times 10^9$.	Per 1 Vol. Per Cent. Ag.
0·872	0	2416	2136	280	361
	−103·83	1570	1266	304	
	−182·73	916	580	335	
	−252·92	359	17	341	
0·960	0	2444	2136	308	353
	−103·83	1596	1266	329	
	−182·73	940	580	360	
	−252·92	380	17	363	
1·586	0	2637	2130	506	350
	−103·83	1806	1263	543	
	−182·73	1161	578	582	
	−252·92	606	17	588	

The general shape of the r . T curves is the same as for the " pure " metals, but the addition of a small amount of the second constituent considerably increases the specific resistance. This additional resistance is approximately independent of the temperature for any concentration in agreement with the relations proposed by Mathiessen and Vogt :—

$$\rho = \rho_m + \xi, \quad \frac{d\rho}{d\mathrm{T}} = \frac{d\rho_m}{d\mathrm{T}}, \qquad . \qquad . \quad (1)$$

in which ρ = specific resistance of dilute alloy, ρ_m = specific resistance of pure metal, ξ = (constant) additive resistance. It will be seen from column 6, Table 14, that the additional resistance is approximately proportional to the amount of silver present.

The electrical resistance of certain other alloys such as manganin, eureka and phosphor-bronze, on the other hand, varies with the temperature in a manner very different from the "pure" metals. Thus these alloys possess a very small negative coefficient of change of resistance at higher temperatures. As the temperature is lowered the resistance reaches a maximum and then decreases approximately linearly at low temperatures, below 100° K. for maganin and below 7° K. for phosphor-bronze, as can be seen from Table 15 :—

TABLE 15

Manganin, Cu 84 per cent., Mn 12 per cent., Ni 4 per cent. (Onnes and Holst.[3])		Phosphor-bronze, Unannealed. (Keesom and v. d. Ende.[4])	
t.	R ohms.	T.	r.
16·5° C.	124·20	4·237° K.	0·7725
−183·0	119·35	3·581	0·7439
−201·7	117·90	2·916	0·7156
−253·3	113·42	2·396	0·6944
−258·0	112·91	1·823	0·6728
−269·0	111·92	1·507	0·6625
−271·5	111·71	1·257	0·6536

This property makes these alloys suitable for use as resistance thermometers at very low temperatures (see Chapter II).

A further type of variation with temperature is exhibited by the class of semi-conductors at low temperatures. Thus the specific resistance of carbon continues to increase with decrease in temperature down to 4° K.

That of germanium shows a minimum at − 116° C. and can be represented by the formula

$$\rho = Ae^{q/T + aT} \quad . \quad . \quad . \quad (2)$$

between − 190° and + 100° C. (Bidwell). Cuprous oxide, according to Vogt,[5] shows a temperature variation of the form $\rho = \rho_0 e^{A/T}$ down to − 190°.

The typical examples of the variation with temperature of the electrical conductivity of various substances given in the above tables may now be compared with the results of recent theoretical investigations. The second column in Tables 10 to 13 contains the calculated values obtained from a semi-empirical formula of Grüneisen :—

$$\rho = C\left\{\frac{20}{x^5}\int_0^x \frac{\xi^4 d\xi}{e^\xi - 1} - \frac{4}{e^x - 1}\right\} \quad . \quad . \quad (3)$$

in which $C = \frac{3}{4}A \cdot \frac{N}{n} \cdot \left(\frac{k}{e}\right)^2 \theta^2$, N = number of atoms per cm.^{3}, n = number of conduction electrons per cm.^{3}, $\xi = \frac{h\nu}{kT}$, $x = \frac{\theta}{T} = \frac{h\nu_m}{kT}$. For very high temperatures, $T \gg \theta$ (θ = Debye's characteristic temperature), the above formula reduces to $\rho = C\left(\frac{T}{\theta}\right)$. For very low temperatures, on the other hand, expression (4) becomes $\rho = 497{\cdot}7\, C\left(\frac{T}{\theta}\right)^5$. The Grüneisen formula thus leads to the same rate of variation of the resistance with temperature at high and low temperatures as Bloch's theory now to be discussed. The agreement between the calculated and (reduced) observed values of r for temperatures much less than θ for the metal in question may therefore also be taken as evidence of the correctness of Bloch's result, viz. $\rho \propto \left(\frac{T}{\theta}\right)^5$ for $T \ll \theta$.

The observed variation of the specific resistance of a pure metal at low temperatures has received a theoretical explanation by the application of the wave mechanics to the problem by Bloch[6] and others. In order to calculate the possible flow of electrons through the crystal lattice of a metal the interaction of an electron with the other particles of the lattice is taken into account by assuming the electron to be moving in a periodic field of potential. The results of the calculation may be illustrated by considering the simplified case of a one-dimensional lattice. It is then found that the energy values, which an electron moving through the lattice can have, form a spectrum of continuous bands of energy states separated by finite intervals of forbidden states. The distribution of the electrons among these energy states is governed by the Fermi statistics which is based on an application of the Pauli exclusion principle to the translatory movements of particles in an enclosure. As a result of the Pauli principle each energy state is completely filled when it is occupied by two electrons, corresponding to the two possible orientations of the electron spin. In a metal all the levels of the lowest band of energy states will be occupied except for a relatively few of the highest energy, there being also a few electrons in the lowest levels of the next band. Under the influence of an applied electric field some of the electrons of the lowest band will make transitions into empty energy states in this band, so producing an electric current. Exchanges between electrons in occupied levels do not result in a current.

In the collisions between the electrons and the ions of the lattice the possible changes of energy and momentum suffered by the electron are limited by certain quantum restrictions. Thus if E_1 is the energy of an electron before and E_2 that after the collision, $E_1 = E_2 \pm h\nu_n$, where ν_n is some possible frequency of the ionic lattice. Since now the energy of the ions decreases as T^4 at low temperatures according to the Debye theory of specific heats, the electrical resistance of a pure metal will decrease rapidly with the temperature. The resistance depends on the number of "effective" collisions per second, those in which the above energy condition can be fulfilled, and on the scattering produced at each collision which is determined by $E_1 - E_2$. These two factors both decrease considerably at low temperatures because the energy of the lattice is then made up largely of low energy quanta. The mathematical formulation of these facts leads to the result $\rho \propto \left(\frac{T}{\theta}\right)^5$ for $T \ll \theta$. At high temperatures, $T \gg \theta$, Bloch's theory indicates that the resistance is proportional to the absolute temperature, $\rho \propto \left(\frac{T}{\theta}\right)$. The expression for intermediate temperatures is more complicated.

The effect of small amounts of impurity can readily be explained by Bloch's theory. The statistical distribution of the additional atoms throughout the lattice can be regarded as a disturbance of the periodicity of the latter. Consequently an additional term has to be added when calculating the scattering of the electrons by the lattice and it can readily by seen that the extra scattering will be independent of the temperature. The excess of the resistance of a dilute alloy over that of the pure metal will thus be independent of the temperature in agreement with observation (Table 14). Provided the concentration of the additional substance is small the increase in resistance will obviously also be proportional to the amount of this substance present.

Wilson [7] has shown that the theory can also account for the behaviour of semi-conductors. If the lowest energy band of a substance is completely filled with electrons and the next band completely empty, the substance will be an insulator if the gap between the two bands is large. If, however, this width ΔE is comparable with kT, a few electrons from the lowest band will be able to make transitions to levels in the next band and so give rise to conductivity in the substance. The variation of the resistance with temperature will, however, be different from that of the pure metals and Wilson has shown that the theory leads to the law, $\rho = \rho_0 e^{A/T}$, in agreement with the experimental results for the typical semi-conductor, cuprous oxide.

SUPERCONDUCTIVITY

In order to study further the question as to whether the residual resistance of an absolutely pure metal really becomes zero at the Absolute Zero or remains finite as earlier work suggested, Kamerlingh Onnes [8] in 1911 determined the resistance of solid mercury at helium temperatures. This metal was chosen because it can readily be subjected to repeated purification. The very important discovery was made that at about 4·2° K. the electrical resistance of mercury begins to diminish rapidly and all measurable resistance vanishes within a temperature range of a few hundredths of a degree. To this new phenomenon the name superconductivity was given. The method employed was the ordinary one of comparing the potential difference across the unknown resistance with that across a known resistance in series with it. The sensitivity of the apparatus was such that a resistance of about 10^{-10} of that present at 0° C. could have been detected. The resistance in the superconducting state was, however, certainly less than that.

The electrical conductivity of many other metals, alloys and metallic compounds has been investigated since 1911 in the cryogenic laboratories of Leiden, Berlin and Toronto. Among the metals examined those in the following table have been found to become superconducting at the temperatures indicated.

With regard to binary alloys it may be stated that superconductivity occurs in (1) alloys of two superconductors, (2) alloys of a superconductor and a non-superconductor in which the crystal lattice of the superconductor is preserved, and (3) in certain intermetallic compounds of one superconductor and one non-superconductor or even of two non-superconductors. The compound Au_2Bi, which becomes superconducting at 1·83° K., is an interesting example of the last class. Meissner [9] has also discovered superconductivity in certain compounds of a metallic and a non-metallic element such as sulphides, nitrides and borides; for example, CuS becomes superconducting at 1·6° K. although it is only a poor conductor at room temperature.

Nearly all the pure metals, with the exception of those of the rare earth group, have been investigated down to about 1·3° K. and a few to lower temperatures, but only those given in Table 16 have been found to become superconducting. It is, however, quite possible that superconductivity may be discovered in some other elements * when the experiments are extended to the range below 1·0° K. attainable by the new methods discussed in Chapter I.

TABLE 16

Substance.	Transition Temperature.
Nb	9·2° K.
Pb	7·26
Ta	4·38
V	4·3
Hg	4·12
Sn	3·69
In	3·37
Tl	2·37
Ti	1·77
Th	1·43
Al	1·14
Ga	1·05
Zn	0·79
Cd	0·6

Fig. 24 gives the "transition curve" for tin, showing the change of resistance with temperature for the three cases of (1) a polycrystalline wire, (2) a wire containing a few large crystals, and (3) a single crystal wire. Each of these curves is reproducible whether traversed from higher to lower or lower to higher temperatures, but the spread of the transition curves is dependent on the strength of the current (de Haas and Voogd [10]).

It will be seen that the residual resistance vanishes within a range of a few hundredths of a degree for the polycrystalline wire. This behaviour is typical of such wires of the pure metals. With a good single crystal the spread of the transition curve is only about 0·002°. It is probable that the transition is actually

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* From measurements on molybdenum-carbon alloys, Meissner concludes that pure molybdenum becomes superconducting at about 1° K., but this has not yet been observed directly.

discontinuous with a perfect strain-free single crystal for infinitesimally small currents.

Since the transition from ordinary conductivity to superconductivity does in general occur over a definite range of temperature it is usual to define the transition temperature as that temperature at which half of the residual resistance present before the transition has disappeared. The temperatures given in the table accord with this definition.

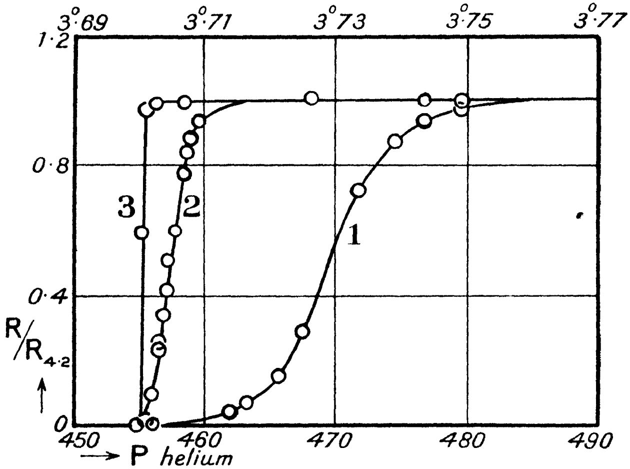

FIG. 24.

If a current is flowing in a circuit containing a resistance R and an inductance L and the e.m.f. is suddenly removed, the current falls to $1/e$ of its original value in a time τ equal to L/R. With ordinary conductors τ is of the order 10^{-5} sec. Since the early determinations had shown that the electrical resistance of a superconductor, even if not strictly zero, could not be greater than $10^{-10} \times R_{0^\circ C.}$, τ in that case would be of the order of days and a current should persist long after the e.m.f. had been removed. This was tested by Kamerlingh Onnes[11] with the aid of the circuit shown in Fig. 25. C was a coil wound with lead wire and immersed in liquid helium. K_1 was a key made of two blocks of lead, one of which was provided with three small conical points. This key was also at the low temperature and served to open or close the superconducting circuit without introducing ordinary resistance.* The circuit was further connected outside the cryostat to a source of current, an ammeter and a galvanometer, as shown. On closing key K_2 a current was sent through C and this was indicated by both the ammeter and the compass needle N, placed outside the cryostat but near C. K_1 was then closed and no change occurred, since there was no measurable difference of potential across K_1. K_2 was next opened and the ammeter read zero, but the compass needle was still deflected, since the current continued to flow through C. K_3 was then closed and finally, hours later perhaps, K_1 was opened. The galvanometer was deflected,

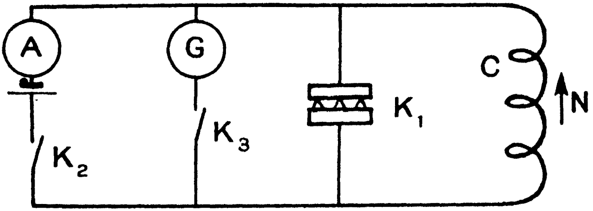

FIG. 25.

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* Since the contact resistance of the plugs of an ordinary resistance box is of the order of $10^{-4}\omega$, it was not at first certain whether K_1 would not also have a contact resistance of this order. It was, however, found to introduce no ordinary resistance. This was later confirmed by Meissner, who also showed that the contact resistance between two different superconductors vanishes at temperatures below the transition points of both metals. This fact is of considerable importance in connection with the theories of the nature of superconductivity.

indicating the current which was originally started by closing K_2 and the compass needle now returned to its undeflected position. This experiment thus demonstrated the existence of currents which persist in a superconducting circuit long after the inducing e.m.f. has been removed.

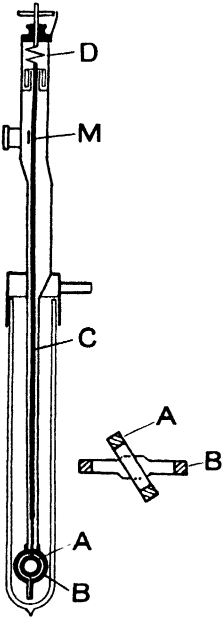

FIG. 26.

A still lower limit was set to the micro-residual resistance of a superconductor by a later experiment of Kamerlingh Onnes and Tuyn.[12] A dynamometer was constructed consisting of two circular lead rings of square cross-section, the outer one fixed and the inner one suspended from a torsion head by means of a spring and glass rod, as shown in Fig. 26. The rings were immersed in liquid helium in the Dewar vessel and the latter was placed between the poles of an electromagnet so that the plane of the rings was perpendicular to the lines of force. The rings were therefore superconducting, the boiling-point of helium at atmospheric pressure at which the experiment was carried out being below the transition temperature of lead. A current was then switched on in the magnet large enough to produce a magnetic field greater than the threshold field-strength of lead (see later). The current was then switched off, and so, when the magnetic field had fallen below the threshold value, currents were induced in the coplanar lead rings. In the actual experiment calculation showed that the currents flowing were 370 and 170 amperes in the outer and inner rings respectively. On account of the vanishingly small micro-residual resistance of the lead no measurable Joulian heat was produced even by these large currents.

The torsion-head was then turned so that the inner ring made an angle of 30° with the outer one. The angle through which the torsion-head had to be turned was greater than 30° on account of the couple due to the action of the currents tending to keep the rings coplanar. By means of the mirror on the suspended system it was possible to observe any change in the angle between the rings resulting from a decrease in the current strengths. It was found that the currents did not decrease by as much as 1 part in 40,000 per hour. A calculation of the time of relaxation τ then showed that the micro-residual resistance of lead at 4·2° K. is less than $10^{-12} \times R_{0^\circ \mathrm{C.}}$. The experiment thus further reduced the maximum possible resistance present in the superconducting state.

A variant of the experiment furnished another result of great importance in connection with the theory of the nature of superconductivity. A hollow sphere of lead was substituted for the inner ring and the experiment carried out as before. It was again found that, after currents had been induced in the lead conductors, a couple, which did not vary by a measurable amount in several hours, was exerted on the suspended system. This meant that the superconducting currents once started in the sphere traversed paths fixed relative to the latter and that they could not be deflected from these paths by any magnetic field less than the threshold field. This conclusion is confirmed by the fact that no Hall effect is shown by superconductors.

Soon after the discovery of superconductivity it was found by Kamerlingh Onnes that if a superconductor is placed in a magnetic field and the latter is gradually increased the ordinary resistance of the wire suddenly begins to return at a definite value of the field strength. The resistance increases with increasing field until the whole of the ordinary resistance corresponding to the temperature of the experiment has returned. The curve so obtained for R against H is quite reproducible, the field strength required increasing as the temperature is lowered more and more below the transition temperature. Fig. 27 illustrates the effect of a longitudinal magnetic field for the case of a polycrystalline wire of tin. The threshold value of the magnetic field is defined as the field required to bring back half of the resistance corresponding to the temperature T in the non-superconducting state. H_T is then connected with T by the relation

$$H_T = a(T_S - T).$$

T_S = normal transition temperature without field. For the case of the pure metals, H_T is generally relatively

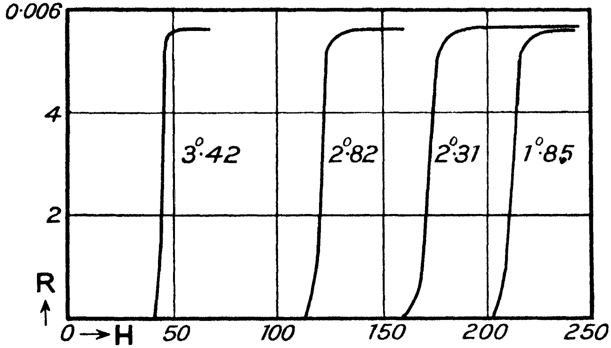

Fig. 27.

small. A few values are given in the following list: Pb, 600 gauss at 4·2°; Sn, 50 gauss at 3·35°; Hg, 14 gauss at 4·12; In, 62 gauss at 2·93°; Tl, 32 gauss at 2·13° (Tuyn and Onnes,[13] de Haas and Voogd[14]). The alloy of lead and bismuth containing 35 at. per cent. Bi is interesting because its threshold magnetic field is very much higher than that of any pure metal. Thus at 4·22° H_T is 18,450 gauss and at 1·97°, 25,700 gauss (de Haas and Voogd). If a solenoid could be wound with wire of this alloy it would be possible to produce magnetic fields of about 20,000 gauss at about 2° K. without any production of Joulian heat. It would only be necessary to immerse the solenoid in liquid helium at this temperature and pass a sufficiently large current through it. One could then partially realise Onnes' suggestion, made before the discovery of the effect of a magnetic field on a superconductor, that very large magnetic fields (100,000 gauss was mentioned) could be obtained in this way.*

Fig. 28 shows the effect of a longitudinal magnetic field on the resistance of a single crystal of tin at 2·92° K.[15] With an increasing field the ordinary resistance returns along a continuous curve as in the case of a polycrystalline wire. When, however, the field is gradually reduced the resistance remains quite constant until some such value as A is reached, when the ordinary resistance disappears discontinuously. The ascending curve is quite definite and reproducible, but the descending curve is not, the discontinuity occurring at A or B or any arbitrary point between them. The effect of the magnetic field thus shows some sort of hysteresis. Fig. 28 is also typical of the behaviour of single crystals of other superconductors. The effect obtained with a transverse magnetic field is somewhat different.

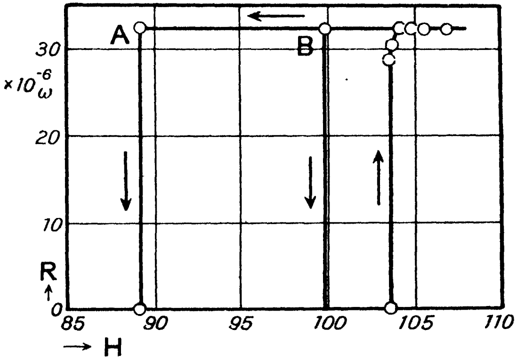

Fig. 28.

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* Experiments on these lines have been commenced by Mendelssohn at Oxford.

It was found by Onnes that if the density of the current through a superconducting wire is raised above a certain critical value the ordinary resistance reappears. Silsbee [16] suggested, and later Onnes and Tuyn established experimentally, that the threshold value of the current is that current which produces the threshold value of the magnetic field at the surface of the conductor. The effect of the current density is thus not a fresh phenomenon in itself.

On investigating the effect of elastic strains on the behaviour of a superconductor, Sizoo and Onnes [17] discovered that tension below the elastic limit raises the transition temperature and that hydrostatic pressure lowers it. These results are unexpected as tensile stress increases the longitudinal resistance and hydrostatic pressure decreases the resistance of an ordinary conductor. The effects are, however, in accord with the empirical fact that a large distance between the atoms in a solid favours superconductivity.

McLennan [18] and Silsbee, Scott, Cook and Brickwedde [19] have shown that the metals which exhibit superconductivity for direct currents are also superconducting with alternating currents of frequencies up to 10^7 per sec. The transition temperature is however somewhat lower than for direct current and to a greater extent the higher the frequency. The significance of the results is however rather obscure at present.

Connection Between Superconductivity and Other Physical Properties

Many attempts have been made to find a connection between superconductivity and other physical properties, but until recently without success. Thus it may be stated briefly that on passing through the transition temperature no change occurs in the dimensions of the crystal-lattice, the elastic properties, the coefficient of expansion, the magnetostriction, the work function and the photoelectric properties. Furthermore, superconthe absolute saturation. The information at present available on this question is derived almost entirely from the work of Weiss and Forrer [1] on various ferromagnetic substances, including iron, nickel, magnetite and cementite, and that of Allen and Constant * on the cubic modification of cobalt.[2] In addition Weiss and Kamerlingh Onnes [3] determined the ratio of the magnetization of iron, nickel and magnetite at room temperature to that at 20° K. for various field strengths. No extensive estimates of the spontaneous magnetization have been made below 100° K., on account of the difficulty in determining accurately the small variation which occurs below this temperature. Thus with most ferromagnetic substances the spontaneous magnetization at 100° K. is within two parts in 100 of the absolute saturation and in some cases within two to three parts in 1000. For the determination of the absolute saturation by extrapolation to Absolute Zero it is therefore generally unnecessary to proceed to lower temperatures than that of liquid air, but measurements below this temperature are definitely desirable to establish the law of approach to saturation. An accurate knowledge of the temperature variation of the spontaneous magnetization at very low temperatures would be of considerable importance from the theoretical point of view.

In the work of Weiss and Forrer and also that of Allen and Constant the magnetization of the substance for some known high field-strength was determined by rapidly withdrawing the specimen—in the form of an ellipsoid—from the field and observing the ballistic throw of the galvanometer in circuit with a pair of coils attached to the pole-pieces of the electromagnet. To obtain the low temperatures the specimen was immersed in a bath of pentane which could be cooled externally by means of liquid air.

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* Apart from the work of Sadron, Peschard and others on various ferromagnetic alloys, which is beyond the scope of the present book to discuss.

The magnetization at any temperature was found for high field strengths to be given by

$$\sigma_{\mathrm{H,T}} = \sigma_{\infty,\mathrm{T}}\left(1 - \frac{a}{\mathrm{H}}\right), \quad . \quad . \quad (1)$$

in which $\sigma_{\mathrm{H,T}}$ is the observed magnetization for a field strength H and temperature T, $\sigma_{\infty,\mathrm{T}}$ is the apparent saturation at temperature T and a is a constant.

The temperature variation of the apparent saturation could be represented by the expression

$$\sigma_{\infty,\mathrm{T}} = \sigma_{\infty,0^\circ\mathrm{K.}}(1 - \mathrm{AT}^2 - \mathrm{BT}^4 - \ldots), \quad . \quad (2)$$

in which $\sigma_{\infty,0^\circ\mathrm{K.}}$ is the absolute saturation, spontaneous magnetization at Absolute Zero, A and B are constants. For iron and cementite the quantity B in (2) is zero and for the other ferromagnetics it is small.

The experimental values of $\sigma_{\infty,\mathrm{T}}/\sigma_{\infty,0^\circ\mathrm{K.}}$ for iron, nickel, magnetite and cementite are given in Table 18 as a function of T/θ, the absolute temperature divided by the temperature of the Curie point * of the substance in question :—

TABLE 18

T/θ.	$\frac{\sigma_{\infty,\mathrm{T}}}{\sigma_{\infty,0^\circ\mathrm{K.}}}$ calc.	Iron.	Nickel.	Magnetite.	Cementite.
0	1·0000	1·000	1·000	1·000	1·000
0·1	1·0000	0·998	0·997	—	0·989
0·2	0·9999	0·991	0·991	0·986	0·978
0·3	0·9974	0·978	0·979	0·960	0·958
0·4	0·9856	—	0·961	0·917	0·927

As far as the law of approach to saturation is concerned the various ferromagnetic substances appear to group themselves according to their crystal symmetry.

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* The Curie point is the temperature at which the spontaneous magnetization of a ferromagnetic substance vanishes. Table 18 was calculated, using the following values of θ : iron, 1047° K. nickel, 631° K. ; magnetite, 858° K. ; cementite, 488° K.

Thus the observations for cubic iron and nickel (and cubic cobalt according to Allen and Constant) fall on the same curve, those for the orthorhombic crystals, magnetite and cementite, approximately on another curve, and those for hexagonal cobalt (Honda and Mazumoto) on a third one.

According to the Weiss theory the spontaneous magnetization σ of a ferromagnetic substance which possesses one effective electron spin moment per atom is determined by the equations

$$\sigma/\sigma_0 = \tanh a, \tag{3}$$

$$\sigma/\sigma_0 = \frac{\mathrm{MRT}}{\mathrm{N}\rho\sigma_{\mathrm{M}}} \cdot a = \frac{\mathrm{T}}{\theta} \cdot a, \tag{4}$$

$$a = \frac{\mu \mathrm{H}}{k\mathrm{T}} = \frac{\mu \mathrm{NI}}{k\mathrm{T}} = \frac{\mu \mathrm{N}\sigma\rho}{k\mathrm{T}}. \tag{5}$$

In the above expressions σ_0 is the saturation magnetization at Absolute Zero, σ_{M} the saturation moment per gram molecule, M the molecular weight, ρ the density, N the Weiss molecular field constant, θ the Curie temperature, μ the magnetic moment per atom, and I the intensity of magnetization per unit volume. By eliminating a between (3) and (4) for the case of no external field for which the expressions in (5) are valid σ/σ_0 can be obtained as a function of T/θ. The values of σ/σ_0 calculated from this expression are given in column 2 of Table 18. It will be seen that the spontaneous magnetization varies more rapidly with the temperature at low temperatures than is given by the simple Weiss theory.

By considering the effect in the wave mechanical treatment of the problem of the " exchanges " between electrons in the neighbouring atoms, Heisenberg [4] was able to give a basis for the explanation of the Weiss molecular field of ferromagnetics. In the absence of an external magnetic field the equations determining the magnetization on the Heisenberg theory are

$$y = \tanh x, \tag{6}$$

$$x = \tfrac{1}{2}\left(\gamma + \frac{\gamma^2}{z}\right) \cdot y + \frac{\gamma^2}{4z} \cdot y^3. \tag{7}$$

The symbols in the above equations have the following meanings :

n = total number of electrons.
n' = number of unpaired electrons.
$y = n'/n = \sigma/\sigma_0$.
$\gamma = zJ_0/kT$, where z is the number of neighbours surrounding each atom and J_0 the interaction integral.

There is assumed to be one effective electron spin moment per atom.

Apart from the terms in γ^2 which arise because of the special assumptions made by Heisenberg with regard to the energy distribution of states corresponding to a particular value of the number of unpaired electrons Heisenberg's theory leads to the same law of variation of the spontaneous magnetization with temperature as equations (3) and (4).

Both these simplified theories require that the spontaneous magnetization shall be the same function of T/θ for all ferromagnetics independently of their chemical nature and crystalline symmetry. This " law of corresponding states " is approximately true, but considerable deviations from it occur at low temperatures and near the Curie point.

Bloch,[5] employing a method due to Slater, has made a calculation of the temperature variation of the spontaneous magnetization at low temperatures which is much more general than Heisenberg's theory. The law of approach to saturation then becomes

$$\sigma = \sigma_0\left(1 - a\left(\frac{T}{\theta}\right)^{\frac{3}{2}}\right), \qquad . \quad . \quad (8)$$

in which a is a constant which has different values according to the crystalline symmetry of the ferromagnetic substance, the numerical values having been calculated for the cases of a simple cubic, a face-centred cubic and a body-centred cubic lattice. The theory thus gives a different law of approach to saturation for substances of different crystalline symmetry in agreement with experiment. The predicted rate of variation of the spontaneous magnetization is, however, again smaller than that actually observed.

Since the Nernst Heat Theorem requires that $\frac{dF}{dT} \rightarrow 0$ as $T \rightarrow 0$ (F is the "free energy") we shall have also $\frac{d\sigma}{dT} \rightarrow 0$ as $T \rightarrow 0$. It is of interest to note that the experimental law of approach to saturation (2) and the various theoretical expressions mentioned above all satisfy this condition, whereas the Langevin expression $\sigma/\sigma_0 = \coth a - \frac{1}{a}$ deduced from the classical theory does not.

The saturation magnetization at Absolute Zero deduced from the observations of Weiss and Forrer and of Allen and Constant is 12,382, 9723 and 3380·8 c.g.s. units per gm. atom for iron, cobalt and nickel respectively. The magnetic moments per atom expressed in terms of the Bohr magneton are then 2·22, 1·7 and 0·606 β.* The value of the gyromagnetic ratio for ferromagnetics shows that the carriers of the magnetic moment are electron spins.† It might therefore be expected that the observed moments would be integral multiples of the Bohr unit, if each atom contributes one or more electron spins. The fact that this is not the case has not yet received a completely satisfactory explanation.

Thus Stoner[6] suggested that a ferromagnetic must be considered as an equilibrium mixture of neutral atoms, ions and free electrons. The atoms and ions contribute to the total moment according to the spin moments of their ground states and the free electrons make no contribution. The suggestion is however unsatisfactory, as the proportion of atoms and ions has to be assumed *ad hoc* and the wave mechanical treatment of the theory of metals shows that no sharp division into atoms, ions and free electrons in the lattice can be made.

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* The Bohr magneton β is equal to $9{\cdot}174 \times 10^{-19}$ e.m.u. or per gram mol. 5564 e.m.u.

† Pyrrohite is apparently an exception, the orbital moment also contributing to the total moment.

Similarly Wolfe [7] postulated that the ferromagnetic is a mixture of atoms in different spectroscopic states (for example, for nickel ^3F and ^1D with spin moments 2 and 0). The known energy differences between the required states are, however, much too great for any appreciable proportion of the atoms to be in the higher state at low temperatures.

Stoner [8] has more recently put forward a theory in which the ferromagnetic metal is considered from the point of view of the Bloch theory of electrical conduction in metals and of the Heisenberg theory of ferromagnetism. The observed values of the atomic moments, it is suggested, correspond to an equilibrium resulting from two opposing tendencies. These are the normal tendency of the electrons in a metal to form pairs and fill up all the lower energy states, each state being completely filled when it contains two electrons of opposite spin, and the tendency of the electrons responsible for the magnetic properties to set parallel in ferromagnetics due to the interaction integral being positive. The resultant atomic moments will then lie between those corresponding to the spin moments of the free atoms (4, 3, and 2 for iron, cobalt and nickel respectively) and zero. The theory has, however, only been presented as yet in a qualitative form.

DIAMAGNETISM

The non-conducting elements and compounds, the molecules of which possess no permanent magnetic moment, are diamagnetic and their molecular susceptibilities (specific susceptibility × molecular weight) are in general independent of the temperature and of the strength of the applied magnetic field. This is, however, not the case with the metals and semi-conductors, the (negative) susceptibility generally increasing as the temperature is lowered and being possibly dependent on the strength of the magnetic field as in the case of bismuth.

The susceptibilities of polycrystalline specimens of most of the diamagnetic elements were determined by Honda [9] and Owen [10] and those of single crystals of a few of the metals by McLennan, Ruedy and Cohen [11] down to the temperature of liquid air. The measurements have more recently been extended to lower temperatures by de Haas and van Alphen [12] (down to 14·2° K.). Table 19 gives some typical results obtained by the latter workers employing a modification of the apparatus shown in Fig. 31.

TABLE 19

$\chi \times 10^6$

T.	Graphite.	Copper.	Silver.	Cadmium.	Lead.	Thallium.	Bismuth.	
							$\perp$ hexag. axis.	$\parallel$ hexag. axis.
° K. 289	−3·0	−0·086	−0·188	−0·183	−0·111	−0·215	−1·48	−1·045
77·2	4·7	0·090	0·191	0·245	0·129	0·246	1·80	—
63·8	4·7	0·091	0·190	0·256	0·131	0·248	−1·80	—
20·4	4·7	0·097	0·19	0·319	0·132	0·255	depends on field	1·20
14·2	−4·7	−0·097	−0·19	−0·326	−0·132	−0·258	—	−1·20

It will be seen that the susceptibility increases with decrease in temperature, the rate of increase becoming smaller as the temperature falls. As the susceptibility of bismuth was found to become dependent on the field strength below 20° K., the phenomenon was examined in more detail with the aid of single crystals with the results shown in Fig. 29, in which the magnetization perpendicular to the hexagonal axis of the crystal is plotted as a function of the magnetic field for the two temperatures 20·4° and 14·2° K. The susceptibility as calculated from these observations is thus a periodic function of the field, the variations being more marked at the lower temperature. On the other hand, the susceptibility parallel to the hexagonal axis is independent of the field down to 14·2° K.

The susceptibility of the diamagnetic metals and semiconductors is the sum of three factors, (1) the diamagnetism of the ions, (2) the Pauli paramagnetism of the conduction electrons, and (3) the Landau diamagnetism of the latter. The contribution due to the diamagnetism of the ions is $\chi_A(\mathrm{I}) = -\frac{Ze^2}{6mc^2}\Sigma\bar{r}^2$ in which Z is the number of atoms per gram atom, e the electronic charge, m the mass of the electron, and $\Sigma\bar{r}^2$ the mean of the square of the radius of the electron orbit summed over all possible values. $\chi_A(\mathrm{I})$ is thus independent of the temperature and field strength.

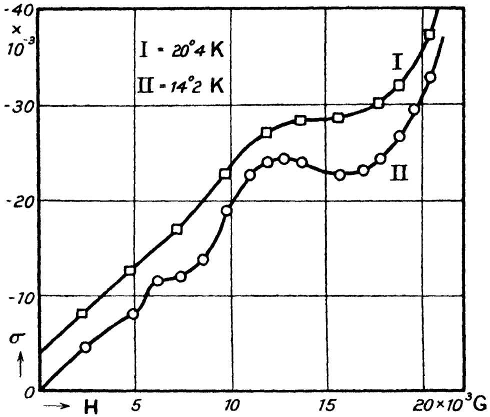

FIG. 29.—The curve for 20·4° K. has been displaced -4×10^{-3} along the σ axis, to avoid confusion with the other curve.

Pauli[13] was the first to show that a "gas" of free electrons, each having a spin moment μ and conforming to the Fermi statistics, shows a weak paramagnetism which is independent of the temperature. A more general calculation by Bloch [14] shows that this contribution to the atomic susceptibility amounts to

$$\chi_{\mathrm{A}}(\mathrm{II}) = +\left[\frac{12m\mu^2}{h^2}\left(\frac{n}{\mathrm{V}}\right)^{\frac{1}{3}}\left(\frac{\pi}{3}\right)^{\frac{2}{3}} - \frac{64\pi^4 \mathrm{V} m^3 \mu^2 k^2 \mathrm{T}^2}{9nh^6}\right]$$
$$= 2{\cdot}20 \times 10^{-14}\left(\frac{n}{\mathrm{V}}\right)^{\frac{1}{3}} - 1{\cdot}03 \times 10^7 \mathrm{T}^2\left(\frac{\mathrm{V}}{n}\right) \quad . \quad (9)$$

n = number of conduction electrons in the volume V.

Since n/V is of the order 10^{22}, the second term is quite negligible at low temperatures and the atomic susceptibility is approximately equal to $+ 10^{-5}$ and independent of the temperature. This result is not materially changed when the conduction electrons are not considered as " free " but as bound more or less loosely to the metallic ions as in Bloch's theory of electrical conduction in metals.

The corresponding calculation for the case of semiconductors (Wilson) gives a different result as the number of electrons in the various " bands " of allowed energies varies appreciably with the temperature. The formula is

$$\chi_{\mathrm{A}}(\mathrm{II}) = +\frac{\mu^2 \pi^{\frac{2}{3}}}{\mathrm{V}\beta}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\frac{1}{2}} e^{-\theta/\mathrm{T}} \text{ for } \mathrm{T} \leqslant \theta, \quad . \quad (10)$$

in which $\beta = k\mathrm{T}_0$, $k\theta = \mathrm{W}_0 - \mathrm{W}_1$ and β, W_0 and W_1 are quantities of the nature of energies connected with the first and second allowed " band " of energies of the conduction electrons. The paramagnetic susceptibility, in this case, decreases exponentially with fall in temperature in agreement with the behaviour of graphite, a typical semiconductor.

When effects due to " spin " are neglected a " gas " of free electrons contributes nothing to the susceptibility on the classical theory. Landau [15] has, however, shown that the quantum theory leads to a weak diamagnetism for such an electron gas, the effect being a consequence of the fact that the angular momentum of the (bent) electron paths in a magnetic field must satisfy certain quantum conditions. The susceptibility so calculated for free electrons is of the opposite sign to (9) and equal to one-third of the first term. It is therefore also independent of the temperature.

Peierls [16] has recently extended Landau's calculation to the case of low temperatures and high field strengths and has shown that the susceptibility is then a function of the applied field. The magnetization should show a series of minima which become more pronounced and more numerous the lower the temperature and the positions of which satisfy the relation $H = \frac{\text{const.}}{m}$, $m = 1, 2, 3$, etc. This is exactly what was observed by de Haas and van Alphen (Fig. 29) for bismuth, but a quantitative agreement cannot yet be obtained between experiment and the theory in its simplest form. The calculations, however, indicate that the effect should be observed most readily with metals having a large diamagnetism and a small number of " free " electrons per atom, such as bismuth, gallium * and antimony and that more minima should appear at the small field strength side of the curve as the temperature is lowered below 14·2° K.

It will be seen that the theory of metals in its simplest form cannot reproduce the temperature variation of the diamagnetism of these substances at low temperatures. It is, however, probable that the experimental results will be satisfactorily explained when the theory of both effects (2) and (3) is extended to the case of bound electrons and the other known facts regarding

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* There is a definite correlation between the variations of the diamagnetism of bismuth with field strength and those of the change of resistance in a magnetic field. As gallium shows similar though not so pronounced phenomena with regard to the latter effect, it is very probable that the diamagnetism of this substance will be found to vary with the field strength at very low temperatures.

the conduction electrons in metals are taken into account.

PARAMAGNETISM

When the atoms or molecules of a substance have a quantum number J which is not zero, they possess a permanent magnetic moment and the substance exhibits paramagnetism. The susceptibility is positive, generally independent of the magnetic field strength and approximately inversely proportional to the absolute temperature.

In order to appreciate the recent advances in theoretical treatment which have greatly added to our knowledge of paramagnetism at low temperatures and much facilitated the interpretation of the experimental results we must quote the general formula from which the susceptibility can be calculated for any given system. By considering the free energy of the system and applying a well-known theorem in statistical mechanics it can be shown that the susceptibility χ per unit mass is given by

$$\chi = -\frac{\mathrm{N}}{\mathrm{H}} \cdot \frac{\sum\limits_{s} \frac{\partial \mathrm{E}_s}{\partial \mathrm{H}} e^{-\mathrm{E}_s/k\mathrm{T}}}{\sum\limits_{s} e^{-\mathrm{E}_s/k\mathrm{T}}} \quad . \quad . \quad (11)$$

In the above expression N is the number of atoms or molecules per gm., E_s the energy of the Sth state of the atom or molecule, and the summation extends over all states which make an appreciable contribution to the susceptibility. The problem of calculating χ thus reduces to that of calculating the possible energy levels of the atom in the presence of a magnetic field.

On account of the Boltzmann factor $e^{-\mathrm{E}_s/k\mathrm{T}}$ the magnitude of the susceptibility and its variation with temperature will depend greatly on the energy separation between the various possible states, a state making an appreciable contribution or not at the temperature T, according as the " height " of the state above the lowest one is small or large compared with kT. In general the possible levels are the components of the lowest multiplet. Thus in the case of the trivalent cerium ion to be considered later, the lowest multiplet is a ^2F, the two components $^2F_{5/2}$ and $^2F_{7/2}$ being separated by an energy difference of 2513 cm.$^{-1}$ * Since this is large compared with kT † only the ground state $^2F_{5/2}$ will contribute appreciably to the susceptibility at low temperatures.

Since, owing to the intervention of other states beside the ground state, the variation of the susceptibility is not in general a strict inverse proportionality to the temperature, it is convenient to characterize the atom or molecule by its " effective magneton number " defined by

$$\mu^2_{\text{eff.}} = \frac{3\chi kT}{N\beta^2} = \frac{3\chi_{\text{mol.}}RT}{(5564)^2},$$

in which $\mu_{\text{eff.}}$ is the effective Bohr magneton number and $\chi_{\text{mol.}}$ the molecular susceptibility. $\mu_{\text{eff.}}$ will in general vary with the temperature and will only be equal to the permanent magnetic moment of the atom or molecule when the substance obeys Curie's law, $\chi T = \text{const.}$

GASES

There exist only two paramagnetic gases which can be investigated at low temperatures, oxygen and nitric oxide. They are of particular interest on account of the great contrast between the temperature variation of the susceptibility in the two cases.

Expression (11), when applied to the case of a diatomic molecule, leads to simple formulæ for the susceptibility in the two limiting cases of the multiplet intervals being very small or very large compared with kT. In the first case the population of the sub-levels of the ground state is independent of the temperature and the formula becomes

$$\chi = \frac{N\beta^2}{3kT}[4S(S+1) + \Lambda^2], \quad . \quad . \quad (12)$$

---

* 1 cm.$^{-1}$ = $1{\cdot}23 \times 10^{-4}$ electron volts = 2·92 calories.

† kT at room temperature = about 200 cm.$^{-1}$.

in which S is the quantum number connected with the total spin moment of the molecule, and Λ that of the component of the orbital angular momentum along the line joining the two nuclei. For a $^3\Sigma$ state, as in oxygen (separation $\Delta\nu$ of the three sub-levels about 1 cm.$^{-1}$), $S = 1$ and $\Lambda = 0$, so that the molecular susceptibility of this gas should be given by $\chi_{\text{mol.}} = \frac{8L\beta^2}{3kT} = \frac{0{\cdot}993}{T}$ (L = number of molecules in the grm. mol.), $\chi_{\text{mol.}}$ should therefore be equal to $3{\cdot}39 \times 10^{-3}$ at 20° and the gas should obey Curie's law, $\chi T = \text{const.}$

The most recent determinations of the susceptibility of oxygen at low temperatures are those of Woltjer, Coopoolse and Wiersma [17] (down to 157° K.), Stössel [18] (down to 136·5° K.) and Wiersma, de Haas and Capel [19] (down to 77·6 K.). While Stössel finds the Curie law to be obeyed accurately, the Leiden workers claim that this is only approximately the case, small deviations occurring which, according to Wiersma and Gorter, are due to the presence of a small number of O_4 molecules in the gas. The observed molecular susceptibility at 20° C. is $3{\cdot}42 \times 10^{-3}$ (W.C. and W.), other values at room temperature being $3{\cdot}48 \times 10^{-3}$ (Wills and Hector) and $3{\cdot}34 \times 10^{-3}$ (Lehrer).

When the multiplet separations of the ground state are large compared with kT, only the lowest sub-level is occupied and the formula for a diatomic molecule becomes

$$\chi = \frac{N\beta^2}{3kT}(\Lambda + 2\Sigma)^2, \qquad . \quad . \quad (13)$$

in which Σ gives the component of the spin moment along the line joining the two nuclei of the molecule. No paramagnetic diatomic molecule satisfying this formula at room temperature is known. The ground state of nitric oxide is a normal $^2\Pi$ state ($^2\Pi_{\frac{1}{2}}$ has a lower energy than $^2\Pi_{\frac{3}{2}}$, separation $\Delta\nu = 120{\cdot}9$ cm.$^{-1}$, $S = \frac{1}{2}$, $\Lambda = 1$) with a multiplet interval comparable with kT. Its magneton number should therefore be 0 at Absolute

Zero as given by (13) and 2 at very high temperatures as given by (12) with intermediate values at intermediate temperatures. The population of the two sub-levels will vary appreciably with the temperature and the expression (11) must be used without the simplifications introduced in deducing (12) and (13). Van Vleck [20] has shown that for this general case the susceptibility is given by

$$\chi = \frac{\theta^2\beta^2}{3kT} \quad . \quad . \quad . \quad (14)$$

with $\theta^2 = 4\left(\frac{1 - e^{-x} + xe^{-x}}{x + xe^{-x}}\right)$ and $x = \frac{h\Delta\nu}{kT}$.

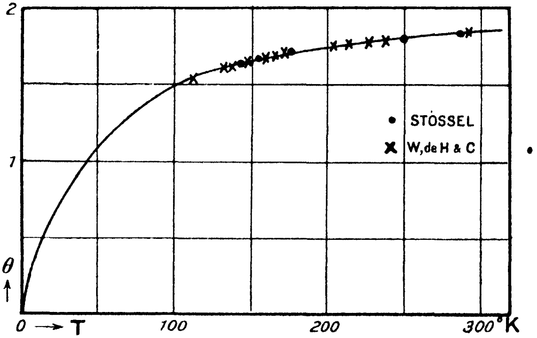

FIG. 30.

θ is therefore the " effective " Bohr magneton number and varies with the temperature, as indicated by the curve in Fig. 30.

The theory has been tested experimentally by Bitter, by Aharoni and Scherrer, by Stössel [21] and by Wiersma, de Haas and Capel.[22] The two last-mentioned series of observations are the most extensive and have been plotted in Fig. 30. It will be seen that the agreement with the theoretical curve is excellent. The " effective " magneton number varies from 1·852 at 292·1° K. to 1·535 at 112·8° K., a striking contrast to the behaviour of oxygen.

Although the effective magneton number becomes zero at Absolute Zero the susceptibility remains finite, because (14) contains a term, characteristic of the quantum mechanics, which is independent of the temperature and of appreciable magnitude in the present case.

SOLIDS

The great majority of the determinations of the susceptibilities of paramagnetic solids have been made on the powdered substance and only these will be considered here. The measurements at low temperatures have almost invariably been made by one of two methods. In the one case a glass or quartz tube is filled with the powder to form a long " rod," one end of which is placed on the axis of the pole-pieces of the electromagnet while the other is situated outside the pole-pieces where the field is almost negligible. A force then acts on the specimen given by $F = \frac{1}{2}\chi m(H_1^2 - H_2^2)/l$ (I), where F is the force, m the mass of the substance, H_1, H_2 the magnetic fields at the two ends of the specimen and l is the length of the specimen. In the other method a small sample of the substance is placed in a non-homogeneous magnetic field when a force acts on it given by $F = \chi m H\frac{dH}{dx}$ (II) in which $\frac{dH}{dx}$ is the gradient of the magnetic field in the direction in which the force is measured. At very low temperatures χ may be a function of H and II is replaced by $F = \sigma m\frac{dH}{dx}$ in which σ is the magnetization per unit mass.

The apparatus used by different observers differs greatly in the methods of measurement of the force and of maintenance of the low temperatures. One typical example may be described. Fig. 31 shows diagrammatically the apparatus used by Gorter, de Haas and van den Handel[23] for the measurement of the susceptibility of potassium chromium alum down to 1·34° K. The specimen A hangs by a quartz rod from one arm of a balance B. The force on A is measured by balancing it against the force produced between a fixed coil C and a movable coil D, attached to the other arm of the balance, when a suitable current is sent through the coils. The specimen is surrounded by a long metal tube attached to the balance case so that the whole forms an air-tight system which can be filled with helium gas to provide the necessary thermal conduction between the cooling bath and the substance under investigation. The lower end of the metal tube is immersed in a bath of liquid helium in the inner Dewar vessel shown and the latter is protected by liquid hydrogen in the outer Dewar vessel. The lower portions of both vessels are of small diameter so that they can be placed between the poles of the electromagnet as shown.*

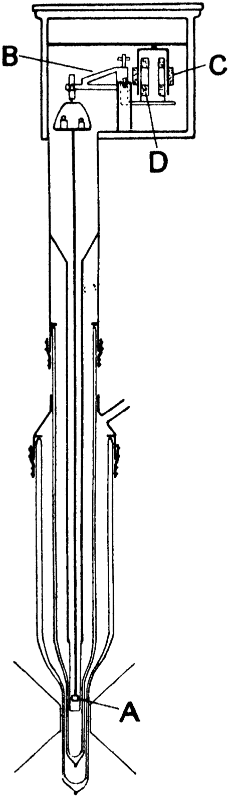

FIG. 31.

The experimental results of the investigation of paramagnetic solids at low temperatures may be briefly summarized as follows. From room temperature down to a temperature which varies from one substance to another but is generally between 20° and 100° K. the susceptibility is given by $\chi(T + \Delta) = \text{const.}$, in which Δ is a constant (the so-called Weiss law). In certain cases Δ is zero and then the substance frequently obeys the simple law down to the lowest temperature investigated. In general, however, the susceptibility deviates from the Weiss law below some definite temperature and may increase either more or less rapidly with fall in temperature than is given by the linear relation between $1/\chi$ and T.

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* With some modifications the method can also be used to measure the susceptibilities of gases by employing a tube filled with gas at high pressure as the "rod" (method I, Woltjer, Coopoolse and Wiersma) or hanging a light sealed bulb in an atmosphere of the gas (method II, Stössel, Wiersma, de Haas and Capel).

The constant Δ is greatly dependent on the nature of the substance being smaller the greater the "magnetic dilution" of the molecule. For example Δ for $Pr_2(SO_4)_3 . 8H_2O$ is 32°, while that of the anhydrous salt is 45°. It can also be positive or negative, being positive in the sulphates of the iron group and negative in the chlorides. The positive sign is, however, the more usual one.

The temperature variation of the susceptibilities of paramagnetic solids, for which Δ is positive, has recently received a satisfactory explanation which we shall now outline very briefly. The discussion will be largely restricted to the compounds of the rare earth metals, as these are more directly amenable to theoretical treatment.

In Table 20 are given the measurements on cerium fluoride (de Haas and Gorter) which may be taken as typical of the results obtained with salts of the rare earths and which will be discussed in detail later. Column 3 shows the validity of the Weiss law with Δ equal to 62 at the higher temperatures and its failure at lower temperatures. (χ' is the susceptibility corrected for the diamagnetism of the anion.)

We will now consider the theoretical interpretation of the observations on paramagnetic solids, making first the simplest possible assumptions, and comparing the results so obtained with the experimental values, so as to determine in what directions the theory must be extended before a complete explanation can be obtained.

Let us first suppose the paramagnetic ions in the solid are completely free, that is, are subject to no external

TABLE 20

CeF_3

T.	$\chi . 10^6$.	$\chi'(T + 62) . 10^4$.
293·0° K.	$11{\cdot}0_9$	39·86
249·0	$12{\cdot}7_1$	39·97
203·8	$14{\cdot}8_9$	39·95
169·5	$17{\cdot}0_8$	39·86
135·2	$20{\cdot}1_4$	40·00
77·53	$29{\cdot}1_6$	40·88
64·08	$32{\cdot}9_2$	41·68
20·42	75·7	62·47
17·15	87·3	69·18
14·48	100·7	77·09

influence but that of the applied magnetic field and that the energy separations between the components of the fundamental multiplet are very large compared with kT. Only the ground state, $J = L - S$ or $L + S$, according as the multiplet is " normal " or " inverted," will then contribute to the susceptibility and, if we neglect a term which is independent of the temperature and is usually small, (11) reduces to

$$\chi = \frac{Ng^2\beta^2J(J+1)}{3kT}, \qquad (15)$$

in which g is the Landé factor and is equal to

$$1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

(15) has been applied by Hund [24] with considerable success to the compounds of the rare earths. By applying certain empirical rules Hund was able to deduce which of the possible states of an ion of a given electronic configuration has the lowest energy and so is the ground state. Column 2 of Table 21 gives the ground states

so deduced for the trivalent ions of the rare earths, assuming that the multiplets are normal in the first half of the group and inverted in the second half. Column 3 gives the Bohr magneton numbers calculated from the data of column 2 by means of formula (15) :—

TABLE 21

+ + + Ion.	Ground State.	$\mu_{\text{eff.}}$ (Hund.)	$\mu_{\text{eff.}}$ (V.V. & F.)	$\mu_{\text{eff.}}$ expt.
La . .	^1S	0·00	0·00	Diamag.
Ce . .	$^2F_{5/2}$	2·54	2·56	2·43, 2·39, 2·27
Pr . .	$^3H_4$	3·58	3·62	3·40, 3·60, 3·52
Nd . .	$^4I_{9/2}$	3·62	3·68	3·60, 3·62, 3·52
Il . .	$^5I_4$	2·68	2·83	—
Sm . .	$^6H_{5/2}$	0·84	1·55	1·56, 1·54, 1·53
Eu . .	$^7F_0$	0·00	3·40	3·60, 3·64, 3·34
Gd . .	^8S	7·94	7·94	7·87, 8·18, 7·78
Tb . .	$^7F_6$	9·7	9·7	9·60, 9·62, 9·35
Ds . .	$^6H_{15/2}$	10·6	10·6	10·50, 10·63, 10·51
Ho . .	$^5I_8$	10·6	10·6	10·45, 10·63, 10·45
Er . .	$^4I_{15/2}$	9·6	9·6	9·43, 9·58, 9·34
Tu . .	$^3H_6$	7·6	7·6	7·52, —, 7·11
Yb . .	$^2F_{7/2}$	4·5	4·5	4·34, 4·57, 4·42
Lu . .	^1S	0·00	0·00	Diamag.

The values in column 3 may be compared with those of $\mu_{\text{eff.}}$ (column 5), deduced from observations on solids for room temperature. It will be seen that with the exception of Sm and Eu there is general agreement. Since, however, (15) necessarily implies the validity of Curie's law, χT = const., good agreement can only be expected for the cases in which Δ is zero or small.

The discrepancies with Sm and Eu are, however, of particular interest, as showing one direction in which the simple theory needs extension. As Van Vleck and Franck [25] have shown, we must discard the assumption that the multiplet intervals are large compared with kT. We may then have contributions to the susceptibility from all the $2J + 1$ components of the fundamental multiplet and we must also retain the term previously neglected. (11) then becomes

$$\chi = \frac{N \sum\limits_{L-S}^{L+S} \{[g_J{}^2\beta^2 J(J+1)/3kT] + \alpha_J\}(2J+1)e^{-E_J{}^0/kT}}{\Sigma(2J+1)e^{-E_J{}^0/kT}} \qquad (16)$$

$E_J{}^0$ is the energy of the state with quantum number J in the absence of a magnetic field, and α_J is the term independent of the temperature which Van Vleck has shown to enter necessarily into the quantum mechanical calculation of χ and which can be interpreted physically as the contribution of the component of magnetic moment perpendicular to the angular momentum vector.

To evaluate (16) we must know the positions of the energy levels, E_J. The actual multiplet intervals of the trivalent ions of the rare earths have not been determined spectroscopically, but they can be calculated from a formula by Goudsmit, giving the over-all width of the multiplet, that is the energy separation between the outermost components, $J = L - S$ and $J = L + S$. The actual intervals between the various components can then be obtained by applying the rule that while the over-all width is proportional to

$$\tfrac{1}{2}[J_{max.}(J_{max.} + 1) - J_{min.}(J_{min.} + 1)]$$

the interval between the components J and $J + 1$ is proportional to $J + 1$. The multiplet intervals for Ce^{+++}, Pr^{+++}, Nd^{+++}, Sm^{+++} and Eu^{+++} calculated in this way are given in Fig. 32.

At low temperatures we are mainly concerned with the interval between the lowest and the next higher level. For the ions mentioned above this interval is 2513, 2113, 1813, 932 and 255 cm.$^{-1}$ respectively. Thus since kT at room temperature is about 200 cm.$^{-1}$, the contribution of the higher level to the susceptibility will be appreciable at this temperature for samarium and europium, but very small for the other ions. Column 4 gives the values of $\mu_{eff.}$ (room temperature) calculated by Van Vleck and Miss Franck, using the more general expression (16). It will be seen that the discrepancies for samarium and europium have now disappeared, while the agreement in the other cases remains as good as before. According to (16) the susceptibilities of samarium and europium compounds will deviate greatly from Curie's law. Their theoretical temperature variations have been calculated by Van Vleck and Miss Franck for a wide range of temperatures.

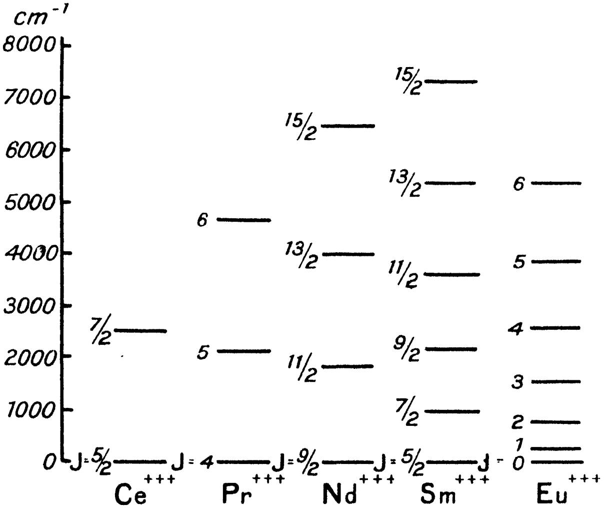

Fig. 32.

We shall not deal with these calculations here, as the measurements on the solid compounds at low temperatures do not agree well with the theoretical values, because there is still another important factor to be considered in the complete treatment of the problem.

We have so far considered the ions to be "free," whereas they are undoubtedly acted upon by relatively large and generally asymmetric electrostatic fields due to the presence of the surrounding atoms or ions in the crystal. The effect of this " crystalline field " will be similar to the Stark effect on free atoms, that is, each level of the ion will be split up into a number of sublevels. Bethe[26] has calculated theoretically the effect of such a field on any given ground state of the ion and has shown that the magnitude of the splitting and the number of components depends on the magnitude and symmetry of the crystalline field. The energies of the components in the absence of a magnetic field having been determined by Bethe's theory, their energies in the presence of a magnetic field can then be calculated and inserted in (11) to obtain the susceptibility. It has thus been found possible to account quantitatively for the variation of $\mu_{\text{eff.}}$ for various rare earth ions over the whole range of temperature investigated by suitably choosing the symmetry of the crystalline field and the magnitude of the constants involved. The theory is too complicated to reproduce here in detail, but some of its general features may be outlined and illustrated with the aid of a few definite examples.

The effect of the crystalline field on the ground state may be summarized as follows : (1) A highly asymmetric field splits up the level into its maximum number of components, $2J + 1$, but when the ion contains an odd number of electrons, i.e. J is half-integral, the components consist of $J + \frac{1}{2}$ pairs of coincident levels (Kramers), or, as it is usually expressed, each component is doubly degenerate. This fact has a very important bearing on the behaviour of μ_{eff} for " odd " and " even " ions at lowest temperatures. (2) In a more symmetric field the number of components may be less than the maximum, due to some of the levels being further degenerate. This will be illustrated later for the particular case of the Pr^{+++} ion. (3) The crystalline field has to a first order of approximation no effect on an S state.* Ions whose ground state is a S state will therefore behave in a solid as if they were " free " and the Curie law should be found to be valid over a wide range of temperature. This is indeed the case with " magnetically dilute " substances containing such ions. Thus, for example, gadolinium sulphate (ground state ^8S) obeys Curie's law for weak magnetic fields down to 1·3° K. (Woltjer and Kamerlingh Onnes [27]) and manganese ammonium sulphate (ground state ^6S) down to 14° K. (Jackson and Kamerlingh Onnes [28]). The magnetic data are thus in entire agreement with the thermal data (p. 61), which shows that the second order splitting of the ground state of the Gd^{+++} ion is of the order of 0·2 cm.$^{-1}$ and so would only cause appreciable deviations from Curie's law at a temperature of about 0·1° K.*

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* When the calculation is carried out to a higher order of approximation a very small splitting is, however, also found for an S state.

As typical examples of these calculations we may now consider the interpretation of the experimental data on CeF_3, $Pr_2(SO_4)_3 . 8H_2O$ and $Nd_2(SO_4)_3 . 8H_2O$ (Gorter and de Haas [29]). The first substance has been theoretically examined by Kramers,[30] the others by Penney and Schlapp.[31] The experimental values of the susceptibility of CeF_3 given in Table 20 can be quantitatively reproduced by assuming a crystalline field of trigonal symmetry in agreement with the crystallographic symmetry of the crystal. The ground state $^2F_{5/2}$ is split up into three (doubly degenerate) components with the following separations: $E_1 = 0$, $E_2 = 113$ cm.$^{-1}$, $E_3 = 489$ cm.$^{-1}$. For the higher temperatures the susceptibility is found to be given by

$$\chi = \frac{Ng^2\beta^2J(J+1)}{3kT} + \frac{K}{T^3}.$$

This can be re-written in the form of the Weiss law $\chi(T + \Delta) =$ const. if Δ is now allowed to vary with the temperature. In this way we obtain the following values for Δ :—

---

* Since an S state ion behaves as if it were gaseous, it is to be expected that crystals containing such ions will be magnetically isotropic independently of the crystalline symmetry of the substance. This has been shown to be the case, for example, with the hexagonal crystal, gadolinium ethylsulphate (Kamerlingh Onnes and Jackson) and various monoclinic manganous and ferric salts (Rabi, Jackson).

$T =$ 50°	100°	150°	200°	300°
$\Delta =$ 51°	60°	61·5°	61°	56°

The slow variation of Δ with the temperature shows why the Weiss law holds for this substance between about 150° K. and 290° K., the reason being obvious from the separations of E_1, E_2, and E_3 given above. Below 150° K. E_2 is only partially excited, while between 150° K. and 290° K. the population of E_1 and E_2 will hardly vary and E_3 is not appreciably excited until a temperature of about 700° K. is reached.

The calculations bring out clearly the fact that Δ is only approximately constant over a limited range of temperature and has no definite physical significance. It is therefore more appropriate to exhibit the effect of the crystalline field by giving the variation of $\mu_{\text{eff.}}$ with the temperature.

$Pr_2(SO_4)_3 . 8H_2O$ and $Nd_2(SO_4)_3 . 8H_2O$ are two salts of similar chemical composition, the one containing an ion with an even number of electrons (Pr^{+++}) and the other an odd number (Nd^{+++}). They both obey the Weiss law at the higher temperatures with Δ equal to 32° and 45° respectively. At lower temperatures, however, the susceptibility of the præseodymium salt increases *less* rapidly with fall in temperature than is given by the Weiss law, the neodymium salt *more* rapidly. It is therefore interesting that Penney and Schlapp have shown that the experimental results for both compounds can be explained on the assumption of a crystalline field of cubic symmetry. The ground state of the Pr^{+++} ion ($^3H_4$) splits up into four components * with an over-all splitting of 389 cm.$^{-1}$, that of the Nd^{+++} ion into three components with an over-all splitting of 834 cm.$^{-1}$. The calculated values of $\mu_{\text{eff.}}$ are given by the curves in Fig. 33. It will be seen that the agreement between the theoretical and experimental values is excellent.

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* To explain the experimental results for anhydrous $Pr_2(SO_4)_3$ it is necessary to postulate a crystalline field of rhombic symmetry and then the ground state splits up into its maximum number of components, i.e. nine.

These curves illustrate clearly the difference at lowest temperatures between ions with odd and even numbers of electrons. In the former case the component of lowest energy is always non-degenerate, with the result that the susceptibility becomes independent of the temperature and $\mu_{\text{eff.}}$ tends to zero at Absolute Zero, while in the latter case, in which the lowest component is doubly degenerate, the susceptibility still varies with the temperature and $\mu_{\text{eff.}}$ tends to a finite value at Absolute Zero. At the higher temperatures the curves asymptote to the values given by (15), i.e.

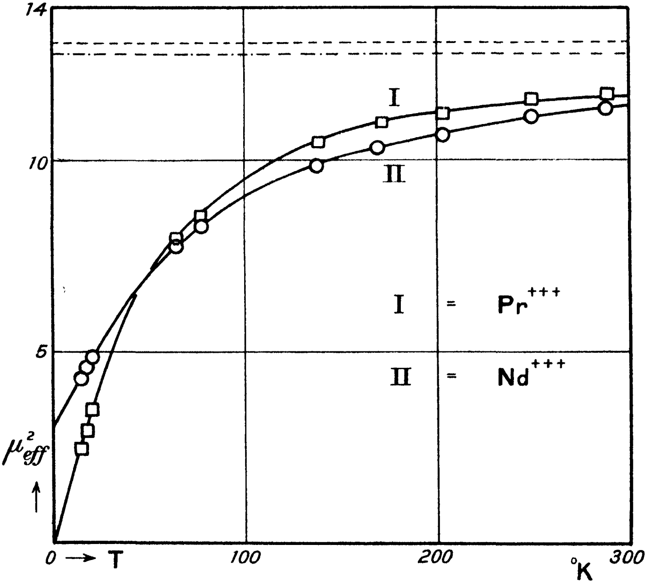

FIG. 33.

$\mu_{\text{eff.}} = 3{\cdot}58$ for Pr^{+++} and $3{\cdot}62$ for Nd^{+++}, shown dotted in Fig. 33. It should be noted that we have only considered the effect of the surrounding atoms on the ground state of the paramagnetic ion. In order to complete the theoretical treatment and in particular to explain the results of Freed,[32] Wiersma and Schultz [33] and Sucksmith [34] on various samarium compounds and of Sucksmith [34] on europium oxide at low temperatures, it will be necessary to calculate also the effect of the crystalline field on the next higher level of the fundamental multiplet.

It will be seen from this brief account of the results of the crystalline field theory that we are now able to account satisfactorily for the variation of the susceptibilities of crystalline paramagnetic compounds over the whole range of temperature over which they have been measured and that the experimental results now furnish valuable information about the crystalline state. The actual energy levels of the paramagnetic ion can be calculated and the symmetry and magnitude of the electrostatic field in which it is situated can be determined. The position of these energy levels can be further tested by measurements of the specific heat, as mentioned in Chapter IV, and in the case of the rare earths * by a study of the absorption spectra of the crystals. All these lines of investigation are being actively pursued at low temperatures and our knowledge of the subject is rapidly becoming a coherent whole.

The phenomena shown by the ions of the iron group are more complicated. The incomplete group of electrons responsible for the paramagnetism is now the outermost group of the ion and, further, the multiplet intervals are much smaller than in the rare earth group. Van Vleck has shown that the effect of the crystalline field is

---

* Crystals of the salts of the rare earths give line absorption spectra, the sharpness of the lines increasing as the temperature is lowered. These spectra have been investigated by Freed, Spedding and others, but the interpretation of them is only in its initial stages.

then to uncouple the L and S vectors and partially or completely " quench " the L moment. The magneton number then lies between that given by writing S for J in (15), i.e. spin moment only, and that obtained from $\chi = \frac{Ng^2\beta^2\{S(S+1)+L(L+1)\}}{3kT}$, i.e. L and S effective but uncoupled from one another, in agreement with the experimental values. The theory has not yet been worked out so completely for the iron group as for the rare earths and the former will not therefore be discussed in detail here.

PARAMAGNETIC SATURATION

When the ions in a crystalline solid can be considered as free and are all in the same energy state, the magnetization per gm. ion is given by

$$\sigma = Ng\beta \frac{\sum\limits_{M=-J}^{M=+J} Me^{-\frac{Mg\beta H}{kT}}}{\sum e^{-\frac{Mg\beta H}{kT}}}, \quad . \quad . \quad (17)$$

in which M takes successively the values J, (J — 1) . . . — (J — 1), — J, corresponding to the possible orientations of the magnetic moment with respect to the direction of the magnetic field. (17) can be transformed into

$$\sigma = NJg\beta \, . \, B\left(\frac{Jg\beta H}{kT}\right) \quad . \quad . \quad . \quad . \quad (18)$$

with $B(x) = \frac{2J+1}{2J} \coth\left(\frac{2Jx+x}{2J}\right) - \frac{1}{2J}\coth\frac{x}{2J}$.

This may be compared with the classical Langevin formula $\sigma = N\mu\left(\coth\frac{\mu H}{kT} - \frac{kT}{\mu H}\right)$. (18) has been plotted in Fig. 34 for the case J = 7/2, together with the classical formula with the same slope at the origin and thus the same $\mu_{\text{eff.}}$.

For small values of $\frac{\mu_{\text{eff.}} H}{kT}$ (18) gives a linear relation between σ and H/T (Curie's law, χ independent of H) and reduces to expression (15). For larger values of $\frac{\mu_{\text{eff.}} H}{kT}$ the curve bends over so that the magnetization is no longer proportional to H but tends more and more to a " saturation " value when the ionic magnetic moments are completely aligned by the field. At room temperature the value of $\frac{\mu_{\text{eff.}} H}{kT}$ is so small even with the strongest magnetic field obtainable that the magnetization lies on the initial straight part of the curve and to observe the approach to saturation it is necessary to extend the measurements to very low temperatures.

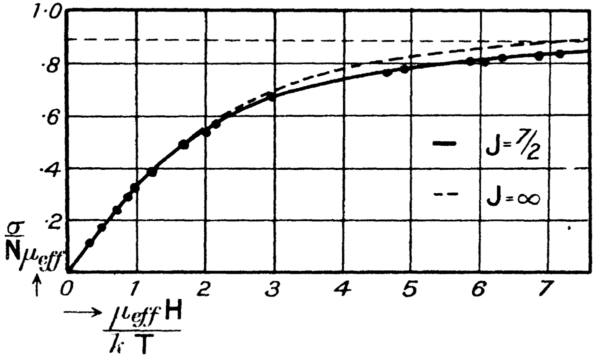

FIG. 34.

Woltjer and Kamerlingh Onnes [35] therefore determined the magnetization of gadolinium sulphate, $Gd_2(SO_4)_3 . 8H_2O$, at temperatures down to 1·31° K. and in magnetic fields up to 22,000 gauss. It has since appeared that the choice was a very suitable one, as the substance is very " dilute " magnetically and the ion Gd^{+++} has a $^8S_{7/2}$ ground state so that the conditions under which (18) is valid are well fulfilled. Definite evidence of saturation was obtained and the experimental points, some of which are plotted in Fig. 34, fitted well on the curve of expression (18) with J equal to 7/2 as required by the $^8S_{7/2}$ ground state. At the highest field strength and lowest temperature used the observed magnetization reached about 95 per cent. of that which would be produced by the complete alignment of the ionic moments.

Gorter, de Haas and van den Handel[36] more recently investigated potassium chromium alum, $K_2SO_4 . Cr_2(SO_4)_3, 24H_2O$, down to 1·34° K. and observed similar saturation phenomena. From the behaviour of this substance at higher temperatures, where it obeys Curie's law accurately, it must be concluded that the magnetic moment of the Cr^{+++} ion is due entirely to the spin moment ($S = 3/2$), the L moment being completely suppressed by the "crystalline field." In agreement with this the observed magnetizations lie on the curve of expression (18) when J is taken as 3/2.

An examination of the quantum theory curve and the classical one discloses a characteristic difference between the two theories. For a given value of $\mu_{\text{eff.}}$ defined as on p. 98 and derived from observations at higher temperatures, the quantum theory gives a saturation moment of $NJg\beta = N(J/J + 1)^{\frac{1}{2}}\mu_{\text{eff.}}$, while the classical theory gives $N\mu_{\text{eff.}}$ Thus in Fig. 34 the asymptote of the classical curve is at $\frac{\sigma}{N\mu_{\text{eff.}}} = 1$, whereas that of the quantum curve is at $(\frac{7}{9})^{\frac{1}{2}} = 0{\cdot}88$, the dotted line. The explanation of the difference lies in the fact that according to the quantum mechanics, the angular momentum of an atom is given by $\{J(J + 1)\}^{\frac{1}{2}} . h/2\pi$ and that in a magnetic field the atom precesses round the direction of the field so that the component of the angular momentum along the field is $(J, (J - 1), \ldots - (J - 1), - J)h/2\pi$. Thus at saturation the total angular momentum makes an angle of $\cos^{-1}\left(\frac{J^2}{J(J + 1)}\right)^{\frac{1}{2}}$ with the field, whereas in the classical case the magnetic moment is aligned parallel to the field when the substance is saturated.

MAGNETIC ROTATION OF THE PLANE OF POLARIZATION

When plane polarized light is passed through a transparent substance placed in a magnetic field the plane of polarization is rotated. With diamagnetic substances the rotation is proportional to the applied magnetic field and independent of the temperature ; with paramagnetic substances it is of the opposite sign, proportional to the field and inversely proportional to the absolute temperature at the higher temperatures. It thus appears that the rotation is proportional to the magnetization of the substance and that therefore it should show saturation phenomena at sufficiently low temperatures in the case of paramagnetic solids. This has been shown to be the case by Becquerel and de Haas.[37] They measured the rotation of single crystals of various minerals such as tysonite (a complex fluoride of Ce, La, Nd and Pd) and of certain pure salts such as dysprosium ethyl sulphate in fields up to 30,000 gauss and at temperatures down to 1·3° K. The phenomena shown by $Dy(C_2H_5SO_4)_3 . 9H_2O$ are the simplest observed and most readily interpretable ; only these will be discussed here.

The theory of the paramagnetic rotation of the plane of polarization has been developed by Kramers on the basis of his calculations of the effect of the " crystalline field " on the energy states of paramagnetic ions in solids. He has shown that if the temperature is so low that all the ions are in the lowest sub-level into which the ground state is split in the crystal the rotation is given by :

$$\omega = a \tanh \frac{\mu H}{kT} + bH, \quad . \quad . \quad (19)$$

in which μ is the effective magnetic moment of the ion in the direction concerned, a and b are constants and the second term is small compared with the first. The curve of ω as a function of H/T is thus similar to those of Fig. 34 and the rotation shows a definite saturation for high values of H/T.

The observations of Becquerel and de Haas on $Dy(C_2H_5SO_4)_3 9H_2O$ at 4·21° K. and 1·62° K. for the case in which the direction of the magnetic field and that of propagation of the light are coincident with the principal axis of the (hexagonal) crystal can be accurately represented by Kramers' formula with an effective magnetic moment of 5·66 β in excellent agreement with the value (5·67 β) derived from susceptibility measurements at these temperatures. It is furthermore the only case in which practically complete saturation has been observed, the curve at 27,000 gauss and 1·62° K. being lower than the asymptote by less than 1 part in 100,000.

Since the ground state of the dysprosium ion is split into eight doubly-degenerate sub-levels by the " crystalline field," the simple formula (19) will no longer hold when the temperature is high enough for the separation between the sub-levels and kT to be comparable, because then the higher sub-levels will also contribute to the observed rotation. This proves to be the case for the observations at 14·12° K. and 20·35° K. Since kT at 14·12° K. is about 10 cm.$^{-1}$, the (as yet unknown) separation, $\Delta\nu$, between the lowest and the next higher sub-level of the dysprosium ion must be less than or at most comparable with that value.

The magnetic rotation of the plane of polarization by crystals at very low temperatures thus enables one to observe the phenomenon of paramagnetic saturation more readily than the rather laborious susceptibility measurements, and further investigation will furnish valuable information regarding the energy states of paramagnetic ions in crystalline solids and the intensity and symmetry of the " crystalline field."

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